GUIDANCE ON SAMPLING AND ANALYTICAL METHODS FOR USE AT CONTAMINATED SITES IN ONTARIO

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Report prepared by:

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Ontario Ministry of Environment and Energy

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Contributors to this Document

Site Assessment and Analytical Methods Work Group Members:

Marius Marsh, Standards Development Branch (Chair)
Ron Lall, Central Region
Sean Capstick, Hamilton District Office
Andy Lewis, Ottawa District Office
Liz Pastorek, Laboratory Services Branch
Al Kuja, Standards Development Branch

Contributors and Reviewers

Editor	Marius Marsh
Ground Water	Ron Lall, George Crawford
Surface Water	George Crawford (Patricia Baulu, Cathy Doehler), Jim Eddie, Bruce Lazerte
Sediment	Deo Persaud, Rein Jaagumagi and Alan Hayton
Soils	Marius Marsh, Ron Pearson
Air	Peter Steer, Dennis Corr, Neil Buonocore, Sean Capstick
Site Assessment	Ron Lall, Andy Lewis, Sean Capstick, Marius Marsh
Analytical	Liz Pastorek, Ijaz Ahmad, George Crawford

Preface

This document provides guidance on a wide range of topics related to site assessment, sampling and analytical methods for use in site clean-ups in Ontario. It is not intended that users of the document read it from cover to cover, but that it help them in their field of interest. Therefore, laboratory personnel will have a greater interest in Section 8 on laboratory methods, whereas field samplers will have a greater interest in the specific media in which they are working. All users should be aware, however, of the interactions between the different activities of site assessment, and they should not work independently. The sections pertaining to project and field Quality Assurance and Quality Control are, for example, pertinent to nearly all users of this document.

Guidance on Sampling and Analytical Methods for Use at Contaminated Sites in Ontario

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Guidance on Sampling and Analytical Methods for Use at Contaminated Sites in Ontario

1. INTRODUCTION AND PURPOSE

This document provides guidance on sampling and analytical methods for individuals involved with site assessment and remediation activities in Ontario. It also outlines procedures that will be considered acceptable to the Ontario Ministry of Environment and Energy (MOEE) regarding sampling and analysis of potentially contaminated sites if the Ministry is requested or decides to review or comment on documentation, or becomes involved in a site clean-up as part of a compliance/audit process. The Ministry recognizes that site clean-ups are highly site specific and that no single protocol or set of procedures is able to cover all conditions. Many sections of this document are, therefore, written to provide general guidance for the conducting of site assessments (i.e. choice of sampling equipment). However, other sections or parts therein for which specifics are required to maintain consistency across the province, are written to assure that certain procedures, specific methods, or clear method principles are utilized.

This document does not cover the sampling and analysis of biological materials nor does it cover other procedures which may be required for the rare circumstances where Ecological Risk Assessments (ERA) may be required. The reader is referred to the portions of the guideline dealing with ERA, and to USEPA and Environment Canada documents referenced therein for information on these topics.

For this document and the guideline it supports, the Ministry has adopted the use of the "Phase 1 and Phase 2" terminology that has become of standard use in the consulting industry over the last few years. The term "Phase 1 Environmental Site Assessment" (ESA) therefore refers to the systematic process of examining existing documents, maps and information provided by knowledgeable individuals pertaining to a site, to determine whether a property is or may be subject to contamination, and to determine the likely nature and location of the possible contamination. A Phase 1 ESA does not normally involve sampling or analysis. The term "Phase 2 Environmental Site Assessment" refers to the process of confirming whether or not suspected contamination exists and defining the nature and extent of that contamination through a sampling and analysis program.

Finally, it should be noted that sections of this document vary in the level of detail provided. This reflects the range of detail available in documents from various program (media) areas of the Ministry. The level of detail provided is not an indication of the relative importance of any particular section. The mention of or reference to brand or trade names for supplies or equipment required to undertake site clean-up is not intended to be Ministry endorsement of that product over similar unnamed products that meet necessary performance criteria/specifications.

1.1 Definitions and Abbreviations

BTEX — Benzene, toluene, ethylbenzene and xylene

Composite Sample — A sample obtained by combining material from two or more spatially separated locations, or in the case of water and air samples, from two or more sampling times. Limits on acceptability of compositing are explained elsewhere in this document.

Duplicate/replicate Sample — A second/additional sample(s) taken in the same manner as the first over the same area and depth increment.

Phase 1 Environmental Site Assessment — The systematic process of examining existing documents, maps and information provided by knowledgeable individuals pertaining to a site, to determine whether a property is or may have been subject to contamination, and to determine the likely nature and location of the possible contamination. A Phase 1 Site Assessment does not normally involve sampling or analysis.

Phase 2 Environmental Site Assessment — The process of confirming whether or not suspected contamination exists and defining the nature, severity, and extent of that contamination through a sampling and analysis program.

Sampling Site — A spatially identifiable location at which discrete or composite samples are taken.

Soil — Loose or unconsolidated material resulting from the breakdown of rock or organic matter by natural physical, chemical and biological processes and which is capable of supporting plant growth. More than 50% of the material by volume must have a particle size of less than 2 mm.

Soil-like — Material meeting the above definition of soil except that it need not be a result of natural processes nor need it be capable of supporting plant growth.

Rock — Aggregations of particles composed of one or more naturally occurring

minerals for which, in total, more than 50% by volume has a particle size of greater than 2 mm.

Rock-like — Material meeting the above definition of rock except that it need not be naturally occurring.

Quality Assurance (QA)

A system of activities and procedures which allows for the producer of a product (i.e. data) to demonstrate that it is constantly producing a product of definable quality. QA consists of those activities that assure that all necessary QC activities were defined and carried out according to protocol. QA is primarily a supervisory responsibility.

Quality Control (QC)

Specific activities conducted for the purpose of maintaining quality in sample collection, analysis, and recording. Primarily a scientific or technical function performed by research or technical staff.

Quality Management (QM)

The process of ensuring that a full and complete QA and QC program is established, that proper evaluation of the total program occurs, and that appropriate actions are taken when satisfactory quality is not being achieved. QM involves the specification of what constitutes acceptable quality, the detailing of the means by which it is determined that the specified quality has been achieved, and the defining of what actions will be taken when the desired quality is not met. QM is normally the responsibility of project management.

TPH — Total petroleum hydrocarbons

2. PHASE 1 ENVIRONMENTAL SITE ASSESSMENTS (ESAs)

2.1 Introduction

The first step in the site assessment process involves the systematic gathering of information to identify actual or potential contamination, or sources of contamination. This is referred to as a Phase 1 Environmental Site Assessment (ESA). A Phase 1 Site Assessment does not normally involve sample collection or analysis.

A Phase 1 ESA may include, but is not limited to the following activities:

- ★ *reviews of property histories through the use of air photographs, insurance maps, land title searches, municipal or provincial archives, regulatory agency records, previous ESA reports, company records, topographic maps*
- ★ *interviews with present and past site occupants, government officials (federal, provincial and municipal), present and past neighbours*
- ★ *site visits to inspect material handling, waste management and storage practices, to investigate for presence of polychlorinated biphenyl (PCBs), or asbestos containing materials (ACM), or to examine building heating and cooling systems and fuel storage locations at operating facilities*
- ★ *sites visits to verify any of the findings or discrepancies noted in the review of historical information or interview process.*
- ★ *geomagnetic or geophysical surveys to gather information for directing subsequent sampling programs.*

The results of the Phase 1 ESA will determine the need for further site investigation. Since soil and groundwater samples are not often collected in a Phase 1 ESA, the importance of accurate and comprehensive gathering of historical site information is critical. This historical information will direct further investigative activities at the site.

Phase 1 ESA results will provide an indication of the need for and, the type of further sampling and analysis required, or it may confirm that the site (soil, sediment, ground/surface water) and\or building(s) are free of contamination and that further investigation is not necessary. If there is evidence of, or reason to suspect, the presence of contamination on the property, the findings of the Phase 1 ESA should provide the required direction for determining which chemical parameters from soil, groundwater or sediment samples to select for analysis in Step 2.

The method, scope and findings of the Phase 1 ESA should be clearly documented in a report which should be retained by the property owner. One possible report format is provided in "Non-Profit Housing Environmental Site Assessment Content and Format Guideline" produced by the Ministry of Housing (1993, revised).

2.2 Summary of Phase 1 ESA Documents

Phase 1 ESA guidance documents have been developed by various organizations. Because of the site specific nature of each Phase 1 assessment, no one particular document can be cited as a single reference, nor is it possible for the MOEE to prescribe a Phase 1 process to cover all site specific scenarios. Rather, this section provides a discussion of existing documents to assist with the selection of the most relevant and appropriate guidance documents for a particular situation.

The following is a list of organizations that have produced guidance on conducting ESAs or related activities. The titles of the guidance documents have been listed, along with the appropriate contact information. The listing of these documents is not intended to be an endorsement of these reports. Similarly, the absence of a report on this listing should not be construed as an indication of non support by the Ministry. The listings are given in alphabetical order of the organization, and the order is not in any way intended to give preference to one document over another.

A brief outline of the information contained in each document is provided to assist the reader in identifying which, if any, of these documents could be of use in meeting their particular need. The list is not exhaustive, but does reflect available information at the time of preparation of this report.

American Society for Testing and Materials (ASTM)
1916 Race St. Philadelphia, Pa 19103
Phone: 215-299-5585 Fax: 215-977-9679

- Standard Practice for Environmental Site Assessments: Phase 1 Environmental Site Assessment Process E 1527 - 93, May 1993

  - provides specific guidance on information gathering activities such as records review, site reconnaissance, and interviews.
  - provides specific information on sources and locations of records, types of information to be examined, and agencies to be consulted.
  - designed to address the *appropriate inquiry* requirements of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) of the US Environmental Protection Agency.

- Standard Practice for Environmental Site Assessments: Transaction Screen Process E 1528 - 93, May 1993

  - provides guidance on putting into practice the environmental site assessment information provided in ASTM E 1527, as applied to commercial real estate transactions.
  - provides a broad list of terminology and a sample questionnaire to guide the information gathering process.
  - designed to address the *appropriate inquiry* requirements of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) of the US Environmental Protection Agency.

Canada Mortgage and Housing Corporation (CMHC)
Research Division, National Office, 682 Montreal Rd, Ottawa, Ontario, K1A 0P7

- Evaluation Protocol for Site Toxicity, CR 6755-4, October 1992

  - provides guidance and direction in support of the June 1992 CMHC policy requiring completion of Phase 1 and Phase 2 ESAs as a qualification for CMHC insurance.
  - provides detailed information on Phase 1 ESA activities, limited information on Phase 2 ESA activities, a discussion on why environmental *audits* are needed by mortgage guarantors, and a questionnaire for gathering historical site use information.
  - includes a list of environmental consultants across Canada

- Advice to Approved Lenders: Policy for Managing Environmental Risks, June 04, 1993

  - provides a detailed outline of Phase 1 ESA activities with limited discussion of Phase 2 ESA activities.

Canadian Council of Ministers of the Environment
326 Broadway St., Suite 400, Winnipeg, Manitoba, R3C 0S5
Phone: 204-948-2090 Fax: 204-948-2125

- National Guidelines for Decommissioning Industrial Sites, CCME-TS/WM-TREO13E, March 1991

  - provides detailed information on the components of Phases 1 to 4 (self defined) of a decommissioning or site clean-up, with specific guidance on site information assessment, including records review and site reconnaissance, site testing, preparation of clean-up plans, implementation of clean-up plans, and establishing clean-up

criteria,
- includes a reference list, and broad discussion of Canadian environmental legislation requirements.

Canadian Standards Association
178 Rexdale Blvd., Rexdale (Toronto), Ontario, Canada, M9W 1R3
Phone: 416-747-4000 Fax: 416-747-4149

- Guidelines for Environmental Auditing: Principles and General Practices, CAN/CSA Z751 January, 1994

- provides advice on the need for environmental management systems to assess environmental performance practices.

- Phase 1 Environmental Site Assessment, CSA Z768. April, 1994

- provides detailed information on Phase I activities including records reviews, site visit, interviews and report table of contents and an outline of Phase 2 activities.
- includes a comprehensive listing of federal and provincial legislation and regulations.

Consulting Engineers of Ontario
86 Overlea Blvd., Don Mills (Toronto), Ontario, Canada, M4H 1C6
Phone: 416-425-8027 Fax: 416-425-8035

- Generally Accepted Standards for Environmental Investigations, April 1993

- provides a model and guidance on an approach which brings environmental management (audit) practices and environmental assessment practices together in assessing environmental liability.
- provides detailed guidance on Phase 1 and Phase 2 ESA's and general guidance on environmental audits including regulatory compliance, environmental management systems, waste minimization, workplace safety hygiene and post construction impact audits and a short discussion of risk assessments.
- includes a reference list

National Ground Water Association
6375 Riverside Drive, Dublin, Oh 43017
Phone: 614-761-1711 Fax: 614-761-3446

- Guidance to Environmental Site Assessments, September 1992

  - provides comprehensive and detailed guidance on records reviews, site walkover process, and interviews in response to *due diligence* initiatives resulting from CERCLA.
  - includes a checklist on pre-acquisition information and detailed guidance on information databases (US).

Ontario Ministry of Housing

Housing Policy Branch, 777 Bay Street, Toronto, Ontario, M5G 2E5
Phone: 416-585-7519 Fax: 416-585-7607

- Non-Profit Housing Environmental Site Assessment Content and Format Guideline, jobsOntario·*Homes*, November 1993 *Revised*

  - provides very comprehensive and detailed guidance on Phase 1 and Phase 2 activities including record sources and reviews, site visits and interviews, tables of contents, guidance on sampling, and identification and screening of remedial options.
  - includes a listing of references and an ESA pre-transaction screen

Phase 1 Site Assessments serve as the basis for the planning of Phase 2 Site Assessments if a potential for contamination is found. Phase 1 assessments must be conducted in a thorough and comprehensive manner such that the information gathered is suitable for use in planning a Phase 2 assessment.

3. PHASE 2 ENVIRONMENTAL SITE ASSESSMENTS

Phase 2 ESAs are undertaken to determine the nature and extent of any potential contamination of a site. This requires that sampling be conducted on the site and may require that sampling take place on adjacent properties where there is potential for off-site migration of contamination from the site. Phase 2 ESAs consist of a planning stage, a sampling and chemical analysis stage, and an interpretation and evaluation stage. It is important that provisions for feedback be incorporated in the planning stage to allow for resampling, should it be necessary, based on interpretation of results.

3.1 Planning Stage

A Phase 1 ESA should be completed prior to designing and conducting a sampling and analysis program for a Phase 2 site assessment. The Phase 1 assessment is necessary to identify potential source areas of contamination, potential pathways and directions of contaminant migration as well as the types of contaminants which may be present. Appropriate sampling should be conducted during the Phase 2 assessment in any areas where the Phase 1 assessment identified the potential for contamination to exist. In addition, a Phase 2 Site Assessment should identify any special conditions existing at or near the site for which an Ecological Risk Assessment could be required. These conditions are detailed in section 6.1 of the Guideline. Actual locations of many of the designated areas referred to in this section are available from District Ministry of Natural Resources offices.

The planning of a Phase 2 ESA is closely linked with quality assurance (QA) and quality control (QC) issues. The reader is therefore referred here to Section 6 of this document, which provides a summary of QA and QC for site assessment projects. The Sampling Planning Guide within that section provides a listing of activities that should be considered in the planning phase of a Phase 2 ESA.

3.2 Sampling and Analysis Stage

Phase 2 ESAs can be carried out using a combination of non-intrusive and intrusive testing techniques. In planning and conducting the assessment, proper use of indicators of contamination can reduce the number of analyses that would otherwise have to be conducted.

3.2.1 Non-Intrusive Testing

Non-intrusive testing is the use of sensing devices to locate underground features, such as buried objects, bedrock, or contaminant plumes, without digging, drilling or the use of sampling probes. The main methods or devices used are electromagnetic (EM), magnetic (M) and ground penetrating radar.

Electromagnetic devices measure changes in electrical conductivity. They can be used to detect underground structures such as storage tanks, and well defined inorganic contaminant plumes where the contaminants alter the electrical conductivity. Interference with EM readings is often created by above ground structures.

Magnetic devices measure local changes in the earth's magnetic field. As such, they can detect underground structures containing iron. Magnetic devices are more sensitive than EM and are not as sensitive to interference from above ground structures.

Ground Penetrating Radar devices measure the change in wavelength of a radar signal that results as the signal travels through the ground and returns back to the device. This change is proportional to the electrical conductivity, the ionic conductivity, and the water content of the ground. These devices can also provide the depth to the anomaly or buried object; however, in most soils they are only useful for detection of near surface objects and contaminant plumes. Since the penetration of the radar decreases as soil water content increases, it is generally only useful under relatively dry soil conditions.

3.2.2 Intrusive Testing

Intrusive sampling is necessary to obtain samples of the relevant media from which accurate analytical determinations of contaminant concentrations can be made. Methods for conducting sampling are described for each media in detail in Section 5. For all relevant media, sampling should extend to below the zone of contamination, or the water table, where technically possible (i.e. bedrock reached). When drilling through confined subsurface layers, appropriate drilling and well construction practices should be used to prevent the creation of conduits for vertical migration of contaminants. All boreholes and wells must be properly abandoned when no longer required for further sampling and/or monitoring.

Methods for obtaining samples for laboratory analysis for the different media are detailed in Section 5 of this document.

3.2.2.1 Determination of Analytical Testing-Needs

Parameters required for analysis should be determined on the basis of the history of the site and the potential for contamination as determined in the Phase 1 Site Assessment. Normally, there should be no need to have samples analyzed for all parameters in the generic criteria tables of the guideline.

Analytical methods used and laboratory quality control and quality assurance procedures should be compatible with the information provided in Section 8 of this document.

3.2.2.2 Recommended Procedures for Field Screening of Soils for VOCs

Field soil VOC (volatile organic compounds) measurements (sometimes referred to as soil vapour measurements) can be used as a screening technique and indicator for volatile organic concentrations in soil. Field soil vapour measurements can be determined using gas detectors. Samples of soil gas can be obtained in accordance with the procedure outlined below, or, alternately, soil gas samples can be collected by driving gas well pipes into the soil and removing the gas with a pump. The field results are not directly comparable with guideline criteria; however, they can be used to aid in determining the extent of contamination and to direct sampling for laboratory analysis. In all cases where field soil vapour measurements are used, confirmatory laboratory analysis must be conducted for volatile components of potential concern identified in the Phase 1 ESA. Field soil vapour measurements can be determined using gas detectors. Samples of soil gas can be obtained in accordance with the procedure outlined below, or, alternately, soil gas samples can be collected by driving gas well pipes into the soil and removing the gas by pump.

During drilling or excavations, soil samples should be collected from each stratigraphic unit and logged for soil type and staining. Care must be taken to minimize losses of volatile components during sampling and storage prior to determining combustible vapour measurements. It is recommended that samples be collected from at least 0.1 m below the surface of the wall face or excavation floor. The split sample method is recommended, with one sample being analyzed for vapours and the other submitted for analysis where appropriate. Discreet samples, as opposed to composites must be taken.

Soil samples for petroleum vapour testing should be placed immediately into 1 litre plastic bags about 1/4 filled and sealed tightly with a nominal headspace. Any lumps of soil within the bag should be gently broken by hand. The soil sample must be allowed to come to room temperature. The soil vapour reading should not be taken until the sample temperature has reached a minimum of 15°C, and a time of 2 hours has elapsed since the sample was bagged. The sample temperature should not exceed the ambient air temperature

where air temperature is greater than 15°C. These time and temperature restrictions are critical to ensure consistency of readings between samples.

The soil vapour reading should be taken using a portable hydrocarbon vapour analyzer (i.e. the Gastechtor Model 1238, or equivalent meter) with a minimum detection limit of 10 ppm. The analyzer is to be calibrated using hexane. At some sites, methane or natural gas may be a significant component of the total soil vapour. To discount the presence of methane, an activated carbon filter may be used in the sampling line. Two samples would then have to be taken at each location: one for analysis without charcoal to give the total soil vapours, and one with charcoal to eliminate all petroleum vapours. Subtraction of the two readings gives the true petroleum vapour levels. (Note that the Gastech Tracetechtor meter is an example of a meter with an internal filter that provides a true reading of petroleum vapours. This meter is equivalent to the Gastechtor Model 1238). Other types of units (e.g. TIP, HNu, etc.) may be acceptable, but vapour readings from different units are not generally comparable (particularly FID vs PID units)

To measure soil vapours, insert the analyzer probe into the nominal headspace above the soil sample by puncturing the plastic bag. Agitate/manipulate the sample gently by hand as the measurement is taken. Record the peak reading registered by the analyzer during the first 15 seconds of measurement.

3.2.3 Location of Sampling Sites

1) Soils

Sampling should be conducted in all potentially contaminated areas identified in the Phase 1 site assessment. A sufficient number of sampling sites should be established to clearly delineate each potential area of contamination. This necessitates that some sampling occur in areas not suspected of contamination. The actual pattern and number of sample sites will depend on the statistical methods chosen for analyzing the resulting chemical data and the chemical parameters being measured, as well as on the above factors. For example, the use of geostatistics as an interpretive tool could produce a different sampling plan than would conventional interpretative methods. The depth(s) of sampling will depend on the nature and location of the source (i.e. underground vs. surface), soil stratigraphy (i.e. sand vs clay), and type of contaminant (i.e. mobile vs non-mobile); however, sampling must extend beyond the zone of contamination.

2) Surface water and sediment

Surface water and sediment sampling sites should be established at upstream and downstream property boundaries. Sediment sampling locations should also be established

immediately downstream of any point source discharges from the property, within wastewater treatment lagoons, and within stormwater ponds receiving stormwater runoff from the property.

3) Groundwater

A minimum of one groundwater monitoring well should be established for each potential source area of contamination. If soil sampling clearly indicates that contaminants from a specific source have not reached the groundwater , then a monitoring well may not be required at that location. To determine the groundwater flow gradient and enable a comparison of the upgradient water quality with the downgradient quality, a minimum of three wells within the same aquifer must be established.

4) Vapours

Vapour monitoring is necessary when it is suspected that volatile contaminants are present. A sufficient number of sampling sites should be established to delineate each potential source area of contamination and to identify the need for further investigation. As well, vapour monitoring locations should be established in all basements and service trenches where there is a possibility of contamination.

The above are minimum requirements intended to provide guidance to proponents. It is recognized that every site is unique and that, in many cases, additional sampling will likely be required to properly delineate the presence and the extent of contamination.

3.3 Interpretation and Evaluation Stage

3.3.1 Determination of Exceedences of Criteria

The means of determining whether or not sample results exceed numeric criteria is critical to the interpretation of the data and to the evaluation process. It also has a direct bearing on the development of a sampling plan. For these reasons, guidance on determining exceedences is included below for the different media.

Soils

If a single sample result or the mean of duplicate/replicate samples exceeds a criterion, that sample is deemed to have failed the criterion, and soil up to the next sample site that passes the criterion is also deemed to be in exceedence of the criterion. This allows the proponent to choose between additional sampling to better define contaminated areas, or to consider all material to the next sampling site as contaminated.

Groundwater

Any single sample result or mean of duplicate/replicate samples exceeding a criterion is deemed to be an exceedence if groundwater quality for that parameter is poorer on site or immediately downgradient from the site than it is immediately upgradient from the site.

Surface Water

If a comparison of upstream and downstream water quality shows any degradation of water quality that is not accounted for by the cumulative effects of sampling and analytical variation, then the difference must be investigated, a cause identified and a remediation plan developed and implemented. This is not meant to necessarily force a clean-up in situations where the Provincial Water Quality Objectives are being met.

Sediments

Where sediment quality criteria exist, any single sample or mean of duplicate/replicate samples that exceeds the Lowest Effect Level requires an examination of the source of the contaminated sediments and, if the source is on-site, a remediation plan should be developed and implemented. Where criteria do not exist, if a comparison of upstream and downstream sediment quality shows any degradation in quality that is not accounted for by the cumulative effects of sampling and analytical variation, then the difference must be investigated, a cause or source identified, and a remediation plan developed and implemented.

Air

Exceedences of air standards, guidelines or relevant criteria occurring during the remediation phase requires an immediate response to reduce the source of the contamination and achieve compliance.

3.3.2 Data Analysis and Interpretation

A guide to data interpretation that is applicable to results from all media is presented in Section 9 of this document. It may be useful to refer to Section 9 for additional information . The process of sampling and interpretation is often iterative, with the results of one sampling program indicating the need for further sampling in specific well defined areas in order to locate sources of contamination or to further define areas that exceed guideline criteria.

4 VERIFICATION

4.1 Confirmatory and Audit Sampling

A verification sampling program is a sampling program to ensure that the remedial work program has been completed and that all contamination has been removed. Verification sampling is not required if the Phase 2 ESA shows that contamination is not present at the site or the Phase 1 ESA does not identify any potential contaminant sources. For all situations where remedial work is undertaken, some form of verification sampling should be conducted.

Two types of verification sampling can be defined. First, confirmatory sampling, which is sampling conducted during the remediation phase to ensure that material is being remediated to the extent and quality desired, is a form of verification sampling. Second, when remediation is complete, audit sampling can be conducted as a form of verification sampling. If the Phase 2 ESA sampling program was complete, there should be no reason to do random testing over the entire site after the remedial work plan is completed. Verification sampling can normally occur as confirmatory sampling during the remedial work plan; hence, a verification sampling program should be developed prior to the start of the remedial work plan. Because of the site specific nature of each remedial work program, it is not possible to develop a generic program for all sites.

Excavation Pits

Where material is being excavated to remediate localized contamination, as in the area surrounding an underground storage tank, material should be excavated until the verification sampling shows that the quality of the remaining material meets the remedial targets.. The sampling program should be expressed as a number of tests per unit volume of material or excavated area with a specified number of duplicates. For example, x samples per square metre of wall area with a duplicate sample taken every y samples. The verification testing should be directed to the areas that are most likely to be contaminated. The number of analytical samples taken in an area will depend on how well the area of contamination has been defined. If the extent of contamination can be easily identified through the use of an indicator, then the verification sampling may be directed to focus on areas of remaining contamination. If the area of contamination can not be easily identified, then a greater number of samples may be required to identify remaining contamination. With the exception of samples for VOC analysis, compositing of materials from the area being represented by the sample (in a manner consistent with section 5.1.3 of this guideline) is preferable to single grab samples.

The use of contaminant indicators such as visual staining, soil types, vapours or odour may be used to direct sampling. It may also be possible to test for a smaller suite of compounds as indicators for the compounds on site; however, all compounds shown as potential contaminants in the Phase 1 Site Assessment must be tested in some samples. If indicators are not available, some randomized method for selection of sampling locations should be introduced in the area where the initial testing indicated contamination.

A confirmatory sampling program has been developed for use at excavations where underground storage tanks that contained gasoline or diesel products are removed. This program uses field soil VOC measurements as an indicator when selecting locations from which to take soil samples for analytical testing. The method is described as follows:

Step 1

Each side wall is divided into a 5 square metre grid pattern and the excavation floor is divided into a 10 square metre grid. A sample is taken from each grid unit for field soil VOC measurement. Additional separate samples should be taken for distinctly different soil horizons or layers. Each sample is then analyzed as outlined in Section 3.3.2.

Step 2

The number of samples to be submitted for analytical testing is determined based on the size of the excavation in accordance with the following table:

Table 4.1A: Minimum Verification Sampling Requirements for Excavation of Underground Storage Tanks used for Gasoline or Diesel Fuels[1, 2]

Floor Area (m^2)	Floor Samples	Sidewall Samples[3]
<25	2	2
>25-50	2	3
>50-100	3	3
>100-250	3	5
>250-500	4	6
>500-750	4	7
>750-1000	5	8

[1] not to be used to determine the number of assessment samples

[2] not intended for excavation pits deeper than 4 m or with floor areas greater than 1000 m^2

[3] sidewall samples should not all be taken from the same wall, and should represent worst-case.

The specific sampling location is chosen based on the field soil VOC measurement determined in Step 1. The samples for analytical testing must be taken from the grids with the highest VOC readings. The samples should not all be taken from the same wall. Compliance with the guidelines is achieved only when all of the following conditions have been met for TPH and BTEX for each excavation.

a) the arithmatic mean of the concentration of the contaminant in all the verification samples is less than or equal to the applicable clean-up criterion for that contaminant, and;

b) no single verification sample exceeds any applicable criterion by more than a factor of three (the vapour readings taken from around this sample location must indicate that the area of soil on the wall or floor exceeding the remediation criteria is less than 10 m^2), and;

c) no more than one verification sample exceeds the applicable criterion (up to 1000 m^2 floor area).

It is noted that the above exceedence criteria apply only to verification sampling for TPH and BTEX analysis for excavations of underground storage tanks used for gasoline or diesel fuels. For all other contaminants and situations, the exceedence criteria outlined in Section 3.3.1 apply. It is also assumed in the use of this procedure that sampling previous to the verification sampling indicated the extent of contamination and that the remediation efforts that occurred were directed at removing the contamination to its full lateral and vertical extent.

Other Remediation Techniques

The sampling program should be conducted in conjunction with the remedial work program to provide feed back to the remedial work. If both programs are properly designed, then this can be an iterative process; remediation is continued until the verification sampling shows that the remediation targets have been met. Indicators may be used in a similar manner to that outlined for excavation pits above.

5. SAMPLING METHODS

5.1 Soil Sampling

5.1.1 Introduction

Within any soil or soil-like material there is inherent variability in chemical properties. The degree of variability differs according to numerous factors, including the size of the area, mode of contamination, the physical/chemical properties of the contaminant, and the soil type. These factors can produce spacial variability that is considerably larger than that encountered in other media. The personnel conducting soil sampling should consider this variability, in addition to the guidance provided in Section 3 on Phase 2 ESAs on sampling locations, such that contamination can be distinguished from natural variability.

5.1.2 Planning Soil Sampling

Purpose and Objectives of Sampling

Prior to sampling a site, the purpose and objectives of the sampling program should be clearly stated. For site clean-ups, the purpose of the sampling is normally to determine the concentrations of contaminants at representative locations across the site, within an acceptable range of accuracy, such that areas where remediation is necessary can be delineated. Adequate planning of the sampling program must occur in order to assure that samples represent the areas and depths desired, that sampling variability is properly determined and accounted for, and that there are sufficient number of samples at the appropriate locations to fulfil the purposes of the sampling. These considerations can be accounted for if specific objectives are defined early in the planning. Such objectives should also include statements of the required quality of data obtained from analytical results and from the overall field program; these are referred to as Data Quality Objectives (DQOs).

Staged Sampling

For most constituents of concern at a site, the movement through the soil is sufficiently slow that concentrations do not change significantly over short periods of time. This allows sampling to be conducted in either one or two stages. A one stage sampling plan results in all samples being collected and analyzed in one survey. A two stage plan begins with a limited sampling plan to determine the parameters of interest, the variability of the chemical parameters, and the location of "hot spots". From the results of the initial

sampling, a second sampling scheme can be planned to define more precisely the areas of concern. Two stage sampling is generally more efficient in that it normally results in better characterization of the site with fewer analyses; however, it may take more time to conduct than one stage sampling. For this reason, it may not be appropriate for spills of mobile materials that require immediate attention.

Background Information.

Compilation of background information on site history, location of structures, storage areas and potential spills from which contamination may have occurred, soil and bedrock types, surface and subsurface water movement, etc., must be conducted prior to planning the sampling. This topic is covered through the conducting of a Phase 1 ESA, as discussed in the previous chapter. The information derived from these assessments is used in developing a sampling plan.

Sampling Plan Designs

Using the available background information, a sampling plan design that is most appropriate for the specific situation can be developed. A sampling design should account for both the likelihood of the original contamination and how the contaminants may have moved over time. The main types of sampling plan designs are as follows;

a) Simple Random Sampling

Locations for sampling are chosen in advance using a proper randomizing method. There is no other restriction; hence, all locations have an equal chance of being sampled for any choice of sampling location, even after an adjacent location has been chosen. This method is rarely used on its own. It would only be useful if there were no indication of probable contaminant sources or distribution, soil type were uniform across the site, and obtaining a uniform distribution of samples across the area were not important.

b) Stratified Random Sampling

Areas likely to have higher concentrations of contaminants, or higher variability of contaminants, are delineated (thus "stratifying" the design), then sampled, normally at a higher frequency than the other areas. Sampling within "strata" is properly randomized, as above. This method is used when knowledge of the site is sufficient to delineate areas that are likely to be contaminated, or likely to

have differences in background concentrations or in variability. If done properly, stratification reduces sampling variability by separating out areas of high and low concentrations and/or variability, and reduces the number of samples required. It defines the areas of greatest interest and provides for reduction of sampling in other areas.

c) Systematic Sampling

Samples are collected in a regular pattern. This may be along specified radii, or on points of a grid. The pattern is chosen according to knowledge of the site. This method normally provides better, or more complete coverage of the area than the random methods. Grid sampling methods are well suited to situations where geostatistical methods will be used in the interpretation of data.

d) Judgement Sampling

In this sampling design sampling locations are chosen solely on judgement, one location at a time. The biases of the sampler become dominant in choosing locations. This method may be useful when the sampler has excellent knowledge of the site and there is thought to be significant contamination present from a number of sources. Where this method is used, it is usually prudent to combine it with other designs.

e) Combinations of the above Methods

The above methods can be combined over the site to give an efficient sampling plan that is most likely to detect contamination and delineate areas of concern.

Planning for Field Sampling

During the planning phase, all the requirements of a proper field sampling program should be detailed and accounted for. The program should not only specify the sampling methods that are to be used for different types of samples, but it should detail the actual field collection and laboratory submission procedures to be used. This assures that procedures are standardized to the extent necessary for comparability of results between sites and between samplings conducted by different personnel. It also minimizes the situations in the field where judgement calls are required by foreseeing many of these situations prior to sampling, and by planning for them. The planning for field sampling should result in sampling personnel having full knowledge of sampling procedures to be used, observations

of field and soil conditions to be recorded, criteria for relocating planned sampling sites, methods of recording site locations, proper containers and labelling of samples, and proper procedures for storing and delivering samples to the analytical lab. The latter necessitates contact at this stage with the analytical lab, especially if analysis for many of the trace organic contaminants is being considered.

The planning for sampling should include considerations of all aspects of the safety of the sampling personnel, as well as of the environment. This includes the potential for exposure to hazardous materials, dangerous equipment, and conditions such as excavations, encountering buried pipes and storage tanks, etc. for which safety protocols should be in place.

5.1.3 Sampling Methods

Table 5.1A lists some advantages and disadvantages of a number of different sampling devices that have been used for soil sampling. The planning of the sampling should consider the type of material likely to be encountered on the site and match this with appropriate sampling devices.

Due to the high degree of small scale variability often encountered in most soils, it is strongly recommended that soil sampling for analysis of potential contaminants other than volatile organics should be conducted by combining a number of samples from the depth of interest into one sample that is representative of both the identifiable sampling site and the depth increment. Samples that are combined into a single composite sample should normally be taken from locations that are no more than four metres apart (i.e. 2 metres radius from the central point of the sampling site). The objective of this composite sampling is to assure that the sample best represents the volume of material nearest the point of interest and which can be treated separately for remediation purposes. The distances between samples making up a composite are limited in order to prevent mixing of contaminated soils with clean soils in the sampling. It is clear that, due to the difficulties of depth sampling, in practice more samples will make up a composite sample where sampling is near the surface than will be the case for sampling at depth. Composite sampling should not be used for collecting samples for analysis for volatile organics, since the mixing process results in the loss of some of these compounds.

For sites where surface soil is expected to remain on site, the 0 - 5 (zero to five) cm depth should be sampled separately from materials at greater depth, since this is the soil that will contribute most to exposure of future site users to any potential contamination. For surface or near surface soils, samples should be collected from within a 2 m radius circle (or equivalent area), with a minimum of 10 cores or grab samples constituting the composite

sample for analysis from each depth increment.

Whatever method is selected for collecting samples, care must be taken to ensure that samples from particular depth increments are not mixed with soil from other depths. Soil horizons displaying different properties should be sampled separately since they may behave very differently with respect to contaminant accumulation and movement. For sampling at depth, composite samples within each borehole should be obtained by combining soil over the specific depth increment or horizon being represented by the sample. Also, a composite sample for each layer consisting of 3 or 4 samples collected within the standard 2 m radius circle is preferable to a sample from a single borehole, but it is recognized that other factors, both economic and site-specific may be limiting. Duplicate samples within a depth increment can be obtained by repeating the composite sampling within the borehole.

It is stressed that composite sampling is conducted to obtain a better representative sample of the specific layer and area of interest, not to combine layers or areas that are different. The composite sampling produces separate samples for analysis for each distinct layer and area; it does not merge samples from different layers or areas.

Collection of control samples taken from nearby areas of similar soil type that are not suspected of contamination is recommended as a useful interpretive tool.

Field Notes

Samplers should be diligent in taking field notes of sampling locations, vegetative cover at the sample site, sample depths, observed soil horizonation and horizon depths, any soil staining or unusual odours observed, or any other observations that could be of potential assistance in interpreting analytical results.

Soil Texture

Soil texture can normally be determined in the field using professional judgement and commonly accepted field methods for soil texture determination. In situations where the sampler determines the soil to be close to the 70% sand cut-off for medium - fine textured materials, samples may be needed for laboratory determination of soil texture (For the purpose of determing the sand fraction, wet sieving methods after dispersion with sodium hexametaphosphate are recommended. Pretreatment with hydrogen peroxide to remove organic matter is suggested for surface soils).

Table 5.1A: Summary of Characteristics of Soil Sampling Devices

Device	Use	Advantages	Disadvantages
Trier	Soft to firm surface soils	Easy to use and clean. Inexpensive	Difficult to use in stony soils, dry sandy soils or hard clays.
Trowel	Soft to firm surface soils	Easy to use and clean. Inexpensive	Difficult to use in hard clays. Difficult to obtain sample that is representative of a specified depth.
Tulip bulb planter	Soft to firm surface soils, 0 - 15 cm	Easy to use and clean. Inexpensive. Uniform diameter and volume. Relatively undisturbed sample suitable for volatile analysis.	Suitable for only one depth. Difficult to use in hard soils or in dry loose soils.
Soil probe or corer (i.e.Oakfield Sampler)	Soft to firm surface soils. 0 - 60 cm.	Easy to use. Core is often relatively undisturbed and suitable for volatile analysis if transferred immediately.	Limited depth capabilities. Difficult to use in hard, stony, or dry sandy soils. Difficult to clean cohesive clays from parts of some designs.
Dutch auger, auger buckets	Surface soils to intermediate depths	Will sample to greater depths than above equipment. Can use in stiffer soils	Depth limited by soil conditions (stones and collapsing sidewalls) . Soil mixing occurs during sampling; therefore, not suited to volatiles. Difficult to clean. Additional care must be taken to assure sample is from proper depth.

Device	Use	Advantages	Disadvantages
Hand held subsoil probes	Surface soils to intermediate depths	As above. Maintains an undisturbed core. Suitable for volatiles.	Depth limited by soil conditions (stones and collapsing sidewalls)
Hand operated power auger.	soil, 15 cm - 5 m	Good depth range. Useful in wide range of soils.	Soil is mixed by auger; therefore, unsuitable for volatiles. Requires two or more operators. Requires gas powered engine, therefore potential for contamination. Difficult to clean. Difficult to use when large stones or rocks present. Care required to assure sample is from desired depth.
Backhoe or power shovel	Soil 15 cm - 5 m	Good depth range for wide range of soils. Allows view of large profile area and wide area for sample collection within a horizon. Allows for collection of undisturbed sample.	Expensive relative to above methods. Highly disruptive.
Split Spoon Sampler	Soil 0 cm - bedrock	Excellent depth range. Maintains reasonably undisturbed core suitable for volatiles. Useful in hard soils.	Relative to surface methods, is expensive. Requires two or more operators. Samples are too disturbed for strength tests.
Thin-Walled (Shelby tube) sampler	Soft soil 0 cm - bedrock	Excellent depth range. Maintains undisturbed core suitable for volatiles (as well as strength tests).	Not durable in rocky soils. Sample can be lost in very soft clays or loose sands below water.

5.1.3.1 Sampling From Material Piles

In some situations it may be necessary to sample from large piles of materials. These situations can pose problems with respect to obtaining samples that are representative of the piles due to the difficulty of getting other than surface samples. Some materials have a tendency for fine and coarse fractions to separate when piled; hence, surface samples are often not representative. The preferred method of sampling piles is for composite samples to be obtained which represent known locations within the pile. Sufficient numbers of samples should be taken at different depths to characterize the depth profile and the lateral spatial variation of the substances of concern. This may result in avoiding large volumes within the pile having to be characterized on the basis of the most contaminated of the samples. Normally, sites should be chosen in a properly randomized manner from locations in the pile, with the exception that known or suspected "hot spots" must be sampled. Where turn around time for sample analysis is appropriate for the operation, piles that are being moved can be sampled in lifts; that is, the next layer to be removed from the pile can be sampled after the previous layer is removed.

5.1.4 Sample Containers and Preservation

The following table shows appropriate materials for sample containers for different classes of compounds for analysis, as well as some comments on sample storage procedures that should be followed.

Table 5.1B: Summary of Appropriate Sample Containers and Storage for Soil Samples.

Parameter Group	Container	Comments
Inorganics	plastic, glass	
VOCs	glass, preferably VOC vials with teflon septum caps	Keep cool (<10 °C). Dry ice is recommended. In field, decant standing water and minimize headspace. Discuss with laboratory prior to sampling.
PAHs and Dioxins/Dibenzo-furans	solvent rinsed, amber coloured glass, foil or teflon lined lids	In field keep cool (<10°C) and out of sun. Refrigerate for storage.
All other organics	solvent rinsed glass, foil or teflon lined lids	In field keep cool (<10°C) and out of sun. Refrigerate for storage. No contact with plastics during sampling.

VOCs must be analyzed as soon as possible.
All other organic analyses should be conducted within 60 days of sample collection.

For storage of samples for organic analysis, it is recommended that refrigeration temperatures be maintained at < 4°C, but it is recognized that many situations can occur where fluctuations to above this temperature are extremely difficult to avoid. Since temperatures slightly above 4°C for very short periods of time are unlikely to significantly affect sample quality, the maximum temperature is set at 10°C, as in Table 5.2D. Some microbiological activity occurs at the above temperatures; therefore, the possibility of breakdown of organics exists. Analysis for organics should occur as soon as possible after sample collection. Samples cannot be stored indefinitely for organic analysis.

5.1.5 Field Quality Assurance and Quality Control

All the principles and procedures outline in Section 7 on Field Quality Assurance and Quality Control should be adhered to.

5.1.5.1 Additional Requirements for Sampling for Trace Organic Chemical Analysis

The basic methodology for soil sampling for trace organics (including pesticides) is the same as that for inorganics described in the preceding sections. However, the following additional procedures should be adhered to.

a) Control of Cross-Contamination

Soil sampling for trace organic contaminants requires special techniques in order to avoid contamination, both from other samples and from sampling equipment and containers. Where potentially dangerous levels of contaminants are suspected, protective gloves made of solvent-resistant material (e.g., latex) should be worn. However, neither gloves nor bare hands should contact the sample directly. Rather than transferring the soil cores from the corer to the sample container with bare or gloved fingers, a stainless steel spatula or knife should be used.

b) Equipment Cleaning Procedure

All sampling equipment which contacts soil directly (i.e. corers, knives) must be scrupulously cleaned between sites. The recommended cleaning procedure is as follows:

1. Remove adhering soil particles by scrubbing with dilute laboratory soap (e.g. Alconox) solution.

2. Rinse thoroughly with distilled water.

3. Rinse with acetone*

4. Rinse with hexane*

   * Where acetone or hexane are potential contaminants for analysis, methanol should be used instead as a rinsing agent.

5. Allow equipment to air-dry before sampling. Do not use a paper towel or cloth.

The soil cores should be placed in a stainless steel bowl, and the soil mixed prior to being placed in the sample jars. The bowl and mixing spoon/rod are cleaned as per the usual wash/rinse procedure described above. Samples for VOC analysis must be placed immediately into the appropriate containers, not mixed or composited.

c) Sample Preservation

The samples, with lids screwed on tightly, must be kept cool (preferably refrigerated, otherwise in coolers out of the direct sunlight) until delivery to the analytical laboratory.

d) Special Requirements for Volatile Organic Compounds

In contrast to sampling for all other compounds, sampling for VOC analysis should be done using discreet samples only, not with composite samples, since the additional time required for the compositing as well as the mixing process results in loss of VOCs. Samples for VOC analysis should be taken at least 0.1 m below the soil surface or pit floor or face. Care should be taken to remove soil particles adhering to the lip of the jar or vial prior to sealing it, and jars must be sealed tightly. Consideration should be given to freezing the samples in the field and ensuring that there are no lengthy delays between sampling and analysis. This, as well as appropriate sample containers, should be discussed with qualified laboratory staff at the receiving laboratory prior to sampling.

5.1.6 Sample Preparation

5.1.6.1 For Inorganic Analysis

Table 5.1C summarizes the sample preparation methods for analysis of inorganic constituents for soil, soil-like, rock and rock-like materials. Soil samples should be spread

out on non-metallic trays in a dust free environment and air dried for 48 hours. If traces of moisture are still visible, air drying should continue until no signs of moisture are evident. Alternately, a subsample can be removed from a well mixed sample and its moisture content determined by oven drying to allow reporting of results on a dry weight basis It is noted that the latter method can result in a small upward bias to the results due to the greater moisture loss. The sample is then disaggregated (not ground) with a mortar and pestle and screened through a 2 mm sieve. The greater than 2 mm fraction is discarded. A sub-sample of the less than 2 mm fraction is then ground until the entire sub-sample passes a 355 µm (#45 US standard testing sieve ASTME -11 specification, Tyler equivalent 42 mesh) sieve. The less than 355 µm fraction is used for all the inorganic analyses except Sodium Adsorption Ratio, pH, Electrical Conductivity, hot water extractable Boron and texture, all of which use the less than 2 mm fraction.

Soil-like materials are to be prepared following the above procedure, except that the entire sample must be ground to pass a 355 µm sieve. All tests except texture, which uses the less than 2 mm fraction are conducted on the less than 355 µm fraction.

Rock and rock-like materials should be ground or crushed to pass a 2 mm sieve and a sub-sample taken from this well mixed sample for analysis, without further grinding. In the case of large monolithic blocks of rock that are not suspected of being contaminated, analysis is not required.

5.1.6.2 For Organic Analysis

When preparing samples for analysis of volatile organic compounds, the soil is neither sieved nor dried, as these processes could result in the removal or loss of some constituents of concern. Instead, a sub-sample is taken from the well mixed sample and its moisture content determined. This value is used to calculate analytical results on a dry weight basis. In taking a sub-sample for organic analysis, care should be taken to avoid including stones or gravelly materials, as these could bias the results due to their disproportionate weight in the small sub-sample.

Samples to be analyzed for volatile organic compounds should be sealed and chilled (<10°C) (the use of dry ice is recommended in the field) until chemical analysis. If grinding is required, as for shales suspected of containing VOCs, then the sample container must be re-sealed immediately following grinding.

Table 5.1C: Summary of Sample Preparation for Inorganic Analyses of Soils

SOIL	SOIL-LIKE	ROCK		ROCK-LIKE
		Large, monolithic blocks	**Composite Material (>50% part. size >2 mm)**	
Sample material sieved to pass 2 mm - all material >2 mm discarded - subsample of <2 mm pulverized to pass 355 µm for bulk analysis - subsample of <2 mm used for SAR, EC, pH, hot water extractable boron, and texture.	All sample material cut/ground/crushed to pass 355 µm for analysis	None (if known or suspected to be contaminated, treat as per Rock-Composite Material)	All sample material cut/ground/crushed to pass 2 mm sieve - no further processing for bulk analysis	All sample material cut/ground/crushed to pass 2 mm sieve - no further processing required

5.2 Groundwater Sampling

Introduction

The objectives of ground water sampling programs are varied and include establishing ambient water quality, meeting regulatory requirements, waste disposal site monitoring, and research directed initiatives. Obtaining a representative sample of the ground water is the goal in all cases; however, sampling protocols to meet that goal will vary for each situation.

Factors which may affect the formulation and outcome of the sampling program include well installation and maintenance, purging methods, use of sampling devices, and filtration and sample preservation. These influencing factors are very important, since the results of the sampling plan provide the basis for further decisions and remedial activities. A short discussion of these topics follows. This information is not intended to provide detailed guidance, but rather to allow for a general understanding. The document "Subsurface Assessment Handbook for Contaminated Sites" (CCME, 1994) provides more detailed guidance on groundwater sampling.

The following sections provide guidance specific to the development and management of a sampling well. The reader is also referred to the next section on surface water (5.3.1 to 5.3.3) regarding additional sampling techniques that may be appropriate. The surface water sampling techniques regarding manual and automated sampling as well as grab and composites may apply and provide valuable information.

5.2.1 Sampling Methods

5.2.1.1 Well Installation

A primary concern in the installation of a monitoring well is the influence of the drilling fluids. Drilling fluids, as used in some but not all drilling methods, assist in removing drill cuttings, preventing borehole caving, cooling and lubricating the drill bit, and act as a seal to prevent fluid loss from the borehole. Water based fluids include fresh water, water with smectite (bentonite clay) additives, water with polymeric additives, and water with both clay and polymeric additives. Air may be used in combination with foams containing strengtheners such as clays and polymers. The introduction of these materials presents opportunities for modification of the ground water chemistry. For example, the high cation exchange capacities of the clays used in drilling fluids may result in metal adsorption during

the well installation process, and result in masking of metal presence in ground water.

The organic content of bentonite fluids, and the presence of organic additives in some fluids may lead to effects on ground water microbial activity. These effects may then influence ground water chemistry by altering the chemical oxygen demand of the ground water system.

When drilling fluids are used in well construction, well development may take a greater period of time. Additional precautions are always needed when fluids are used in well construction because of the increased potential for an effect on the ground water system. Table 5.2A presents a short summary of drilling methods and the potential effects on water samples.

5.2.1.2 Well Trauma

Well trauma may best be thought of as a function of the difference between the natural groundwater geochemistry and that of the substances introduced during the well installation process. These are substances which are independent of those which may be present from fluid drilling practices. Substances such as gasoline, hydraulic fluid and lubricants are present on all drill rigs and, therefore, at all drill sites. Material may be transferred to ground water from gloves, drill rod lubricants, degreasing fluids used to clean screens and casings, or as a result of affected surface soils falling into the hole.

The use of bentonite clays as the annular seal, the presence of silica sands, and cement grouts may all influence the presence and concentrations of various cations. Changes in chemical equilibrium will affect the concentration of any contaminants which complex with these ions. Once present, the time required for ground water equilibrium conditions to again be achieved may be months or years. Ongoing sample collecting may actually serve to prevent equilibrium conditions from being re-established.

5.2.1.3 Well Purging

Water standing in a well is not thought to be representative of the conditions within the water bearing formation. Standing well water in contact with the well construction materials for an extended period of time will have differences in temperature, pH, redox potential, and dissolved solids compared to the formation water. Well purging is used to eliminate the potential for an effect from these factors. Well purging, therefore, may be the single most influencing factor in the water sampling process.

Over pumping or over purging a well may lead to de-watering problems, turbidity problems, and dilution and movement of contaminants. These all lead to inaccurate

measurements of aquifer conditions.

Reduction of the volume of standing water during well purging may result in decreases in well pressure conditions. This pressure change may allow precipitation of cations as dissolved gases come out of solution, thereby modifying the water chemistry. The purging method and volume of water to be removed are, therefore, important considerations in any sampling program.

Options for purging wells include:

a) removal of a prescribed number of well volume equivalents[1];

b) continued removal until certain field measured parameters have stabilized;

c) allowing hydraulic performance of the well to dictate purging volumes and rates.

It is not possible to prescribe a specific purge volume for all situations. This depends on the objective of the sampling program, the chemistry being dealt with and the purge technique being employed. Numbers may vary from 1 to 20 bore volumes, and purging may be done at the static level elevation or at the screen base elevation when pumps are used. The location of the purge point may influence the number of purge volumes needed to obtain representative samples.

Parameters such as temperature, pH, Eh, and specific conductance may be used to establish stability trends and, therefore, representative sampling conditions. Measurement of these parameters may not be indicative of representative sampling conditions when volatile organic chemicals are of primary concern.

Knowledge of the formation transmissivity and well casing diameter may be used to determine the purge rate and time required to collect representative samples. In addition, multiple samples taken over a purging period may be used to identify trends and ensure that a point of stability was reached during the sampling program.

During a ground water monitoring programme, it is important that both purging and sampling methods be consistent.

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[1] volume of water above the top of the well screen

5.2.1.4 Sampling Devices

The most important consideration in designing and completing a successful investigation program may be the choice of sampling device. The sampling device has the potential to alter the chemical composition of the ground water sample, and as such the materials used, method of operation, ease of maintenance and field operation are some of the considerations which go into determining which sampling device is appropriate for the exercise. Table 5.2B provides a brief summary of some of the characteristics of commonly used sampling devices. Table 5.2C provides a comparison of the advantages and disadvantages of some of these sampling devices.

5.2.1.5 Abandoning of Wells

All wells must be abandoned in a proper manner such that there is no safety hazard remaining after abandonment and such that the well does not provide a route for contaminant migration to the groundwater.

5.2.2 Sample Filtration

There are situations for which sample filtration is required prior to analysis, and there are circumstances where samples should not be filtered. Filtration may affect the chemical composition of a sample by alteration of the physical state through removal of particulate and any adsorbed material. On the other hand, dissolved phase components may be the only feature of interest in the sample, and clear samples may be essential to the analytical technique of the apparatus being used.

Sample filtration leads to additional atmospheric contact and to the potential for loss of volatile components and sample oxygenation. This may in turn lead to precipitation and removal of metals previously in solution. The filter papers or filtration devices may also serve to influence the integrity of the sample.

Specific guidance on the need for filtration may be obtained from analytical laboratories and will be a function of the need to eliminate potential interference caused by the presence of particulate in samples. Some additional information that is useful to this question is provided in the laboratory methods section of this document (Table 8.4.7). Long term studies requiring strict controls and subject to seasonal variations in water quality will benefit from sample filtration whether in the laboratory or in the field.

In deciding whether or not it is appropriate to filter water samples prior to analysis, it

is helpful to be aware that the ODWOs, upon which many of the groundwater criteria are based, apply to the water that is being consumed. Thus, for example, if a domestic drinking well is being sampled, then it should be sampled at the tap and, wherever possible, not filtered.

5.2.3 Sample Preservation

The preservation of samples is a measure designed to stop or slow the ongoing effects of chemical and biological change once a sample has been collected. Since sample analysis is very specific, the preservation techniques required to ensure sample integrity are also specific. Table 5.2D provides a list of containers, preservatives and holding times for a variety of parameters. A full discussion of aqueous chemistry is beyond the scope of this document, however, an appreciation of the complexities may be gained from examination of Table 5.2D. Preservation methods used for samples must be chosen with care. Preserving a sample for one or a group of parameters may render it unsuitable for other parameters.

Table 5.2A: Effects of Drilling Methods on Water Samples

Method	Advantages	Disadvantages
Air rotary	· Drilling fluid is not always used, minimizing contamination and dilution problems	· When more than one water-bearing zone is encountered and hydrostatic pressures are different, flow between zones occurs after drilling is completed but before the hole is cased and grouted · Oil from compressor may be introduced to geologic system · Use of foam additives which contain organic materials can interfere with both organic and inorganic analyses
Mud rotary		· Drilling fluid which mixes with formation is difficult to remove and can cause contamination · Fluid circulation can cause vertical mixing of contaminants · Drilling fluids and additives can interfere with subsequent water quality analyses · Lubricants may cause contamination
Bucket auger	· No drilling fluid is used, minimizing contamination and dilution problems	· Large diameter hole makes it difficult to assure adequate grouting · Must continuously add water in soft formations
Solid stem auger	· No drilling fluid is used, minimizing contamination and dilution problems · Can avoid use of lubricants	· Because auger must be removed before well can be set, vertical mixing can occur between water-bearing zones · Can cause vertical mixing of both formation water and geologic materials
Hollow stem auger	· No drilling fluid is used, minimizing contamination and dilution problems · Can avoid use of lubricants · Formation waters can be sampled during drilling · Well can be installed as augers are removed, decreasing interaction with water from higher water-bearing zones	· Can cause vertical mixing of geologic materials · Can cause vertical mixing of formation waters if augers are removed before well is installed
Cable tool	· Little or no drilling fluid required	· Contamination is possible if drilling fluid is used · Slight potential for vertical mixing as casing is driven
Jetting	· May be only alternative where rig cannot get in	· Large quantities of water or drilling fluid are introduced into and above sampled formation · Cannot isolate zone with a grout seal

Table 5.2B: Summary of Characteristics of Sampling Devices Available for Small Diameter Monitoring Wells

Device	Minimum Well Diameter cm (in)	Approx. Maximum Sampling Depth (m)	Typical Sample Delivery Max. Depth	Flow Controllability	Materials[a] (Sampling Device Only)	Potential for Chemical Alternation	Ease of Operating, Cleaning and Maintenance
Bailers	3.8 (1½")	Unlimited	Variable	Not applicable	Any	Slight-moderate	Easy
Syringe samplers	3.8 (1½")	Unlimited	0.75 L	Not applicable	Stainless 316, Teflon or polyethylene/glass	Minimum-slight	Easy
Suction-lift (vacuum) pumps	3.8 (1½")	8	Highly variable	Good	Highly variable	High-moderate	Easy
Gas-drive samplers	2.5 (1")	90	0.75 L/min	Fair	Teflon, PVC, polyethylene	Moderate-high	Easy
Bladder pumps	3.8 (1½")	120	2 L/min	Good	Stainless 316, Teflon/Viton, PVC, silicone	Minimum-slight	Easy
Gear-drive submersible pumps	5 (2")	60	2 L/min	Poor	Stainless 304, Teflon, Viton	Minimum-slight	Easy
Helical rotor submersible pumps	5 (2")	40	1 L/min	Poor	Stainless 304, EPDM, Teflon	Slight-moderate	Moderately difficult
Gas-driven piston pumps	3.8 (1½")	150	0.9 L/min	Good	Stainless 304, Teflon, Delrin	Slight-moderate	Easy to moderately difficult
Inertial Pump	1.25 (1/2")	90	Highly variable	Good	Delrin Acetal, Stainless Steel	Slight-moderate	Extremely easy

Modified from Nielsen and Yeates, 1985

[a] Materials dependent on manufacturer and specification of optional materials.

Table 5.2C: Advantages and Disadvantages of Several Types of Groundwater Sampling Devices

Advantages	Disadvantages
Bailers	
· Bailers can be constructed of virtually any rigid or flexible material, including those materials that are inert to chemical contaminants.	· In deep wells, well purging can be difficult and therefore labour- and time-consuming.
· Bailers are mechanically very simple, and thus are easily operated and disassembled for cleaning and repair.	· If the line used with the bailer is not a "non-contaminating" line and is not dedicated to a single well or is not adequately cleaned after each sampling event, cross-contamination between wells can result.
· Bailers are, in comparison with other sampling devices, very inexpensive, making them feasible for dedicated installation in monitoring wells.	· Aeration, degassing, and turbulence can occur while lowering the bailer through the water column or while transferring the sample from the bailers to the sample container.
· Bailers can be used to sample water from wells of virtually any depth.	
· Bailers require no external power source, and are lightweight and highly portable.	· The person sampling the well is susceptible to exposure to any contaminants in the sample.
· Bailers made of flexible material will pass through nonplumb wells.	· Bailing does not supply a continuous flow of water to the surface.
· Bailers can be made to fit any diameter well, and can be made virtually any length to accommodate any sample volume.	· It may be difficult to determine the point within the water column that the sample represents.
· Bailers can provide a "cut" of immiscible contaminants (i.e., petroleum hydrocarbons) from the top of the water column in a well. Transparent bailers are usually used for this purpose.	· Bailer check valves may not operate properly under certain conditions (e.g., high suspended solids content and freezing temperatures).
	· The "swabbing" effect of bailers that fit tightly into a well casing may induce fines from the formation to enter the well, especially if the well has been poorly developed.

Table 5.2C (con't)

Advantages	Disadvantages
Syringe Devices	
· The sample taken with a syringe device does not come into contact with any atmospheric gases and is subjected to a very slight negative pressure, thus neither aeration nor degassing of the sample should occur. · Samples can be collected at discrete intervals and at any depth. · Syringes can be made of inert or nearly inert materials. · Syringe are not restricted to the limits of suction lift. · The syringe can be utilized as the sample container, thus removing the possibility of cross-contamination between wells. · Syringes are inexpensive, highly portable, and simple to operate. · Syringe devices can be used in wells as small as 3.2 cm (1¼ in). inside diameter.	· Syringes are inefficient for collecting large volume samples. · Syringes cannot be used to purge a well. · Syringes are relatively new in the application, therefore they may not be as readily available as other sampling devices. · Sample contamination by components of "homemade" sampling devices is possible unless materials are carefully selected. · The use of syringe is limited to water with a low suspended solids content. · Some leakage has been found to occur around the plunger when syringes are used to sample water containing high levels of suspended solids.

Table 5.2C (con't)

Advantages	Disadvantages
Suction-Lift Pumps	
· The flow rate of most suction lift pumps is easily controlled. · Suction-lift pumps are highly portable and readily available. · Most suction-lift pumps are inexpensive in comparison to other sampling devices. · The pump does not contact the sample - only the tubing must be cleaned (peristaltic pump only). · Suction-lift pumps can be used in wells of any diameter, and can be used in nonplumb wells.	· Sampling is limited to situations in which the potentiometric levels is less than 25 feet below the surface. · A drop in pressure due to the application of a strong negative pressure (suction) causes degassing of the sample and loss of volatiles. · An electric power source is required for peristaltic pumps. · The gasoline motor power source used for most centrifugal pumps provides potential for hydrocarbon contamination of samples. · Pumping with centrifugal pumps results in aeration and turbulence. · Centrifugal pumps may have to be primed, providing a possible source of sample contaminations. · Low pumping rates of peristaltic pumps make it difficult to purge the well bore in a reasonable amount of time. · Where the sample comes in contact with the pump mechanism or tubing, the choice of appropriate materials for impellers (centrifugal pump) or flexible pump-head tubing (peristaltic pump) may be restrictive.

Table 5.2C (con't)

Advantages	Disadvantages
Gas-Drive Devices	
· Gas-drive devices can be utilized in wells of 3.2 cm (1¼ in). inside diameter.	· If air or oxygen are used as the driving gas, oxidation may occur (causing the precipitation of metals), gas-stripping of volatiles may occur, or CO_2 may be driven from the sample (causing a pH shift). Consequently, air-lift sampling may not be appropriate for many chemically sensitive parameters.
· Gas-drive devices are highly portable for most sampling applications, and are inexpensive.	· An air compressor or large compressed-air tanks must be transported to deep sampling locations, reducing portability.
· Discrete depth sampling is possible.	· Application of excessive air pressure can rupture the gas entry or discharge tubing.
· Gas-drive devices can provide delivery of sample at a controlled, nearly continuous rate.	· Devices installed permanently in boreholes without casing are difficult or impossible to retrieve for repair; proper installation and operation may be difficult to ensure.
· The use of an inert driving gas (i.e., nitrogen) minimizes sample oxidation and other chemical alteration.	
· Devices can be installed permanently in boreholes without casing.	
· Multiple installations can be achieved in a single well or borehole (either temporarily or permanently installed).	
· Gas-drive devices can be constructed entirely of inert materials.	
· The depth from which samples can be taken with gas-drive devices is limited only by the burst strength of the materials from which the device and tubing are made.	

Table 5.2C (con't)

Advantages	Disadvantages
Gas-Operated Bladder Pumps	
· Most of these pumps have been designed specifically to sample for low levels of contaminants, so most are or can be made of inert or nearly inert materials.	· Deep sampling requires large volumes of gas and longer cycles, thus increasing operating time and expense, and reducing portability.
· The driving gas does not contact the sample directly, thus problems of sample aeration or gas stripping are minimized.	· Check valves in some pump models are subject to failure in water with high suspended solids content.
· Bladder pumps are portable, though the accessory equipment may be cumbersome.	· Most currently available pump models are expensive, though prices are highly variable.
· The relatively high pumping rate (in comparison with other sampling devices) allows well purging and large sample volumes to be collected.	· Minimum rate of sample discharge of some models may be higher than ideal for the sampling of volatile compounds.
· The pumping rate of most of these pumps can be controlled rather easily to allow for both well purging at high flow rates and collection of volatile samples at low flow rates.	
· Most models of these pumps are capable of pumping lifts in excess of 60 m.	
· These pumps are easy to disassemble for cleaning and repair.	
· Most models of bladder pumps are designed for use in wells of 5 cm (2-in) inside diameter; some are available for smaller diameter wells.	
· Large diameter bladder pumps (i.e., 8.25 cm (3¼in) outside diameter) are available for large diameter monitoring wells.	

Table 5.2C (con't)

Advantages	Disadvantages
Gear-Drive Electric Submersible Pumps	
· These pumps are constructed of inert or nearly inert materials; therefore, they are suitable for sampling organics when optionally available Teflon discharge line is employed.	· There is no control over flow rates; therefore, it is not possible to adjust from a high pumping rate for well purging to a lower rate required for sampling of volatiles.
· These pumps are highly portable and totally self-contained, except when auxiliary power sources are employed.	· Sampling in wells with high levels of suspended solids may necessitate frequent replacement of gears.
· These pumps provide a continuous sample over extended periods of time.	· The potential for pressure changes (cavitation) exists at the drive mechanism; however, this has not been adequately evaluated.
· Models are available for both 5 cm (2-in.) and 7.5 cm (3-in.) (or larger) inside diameter wells.	
· High pumping rates are possible, making it feasible to use the pump for both well purging and sampling.	
· Reasonably high pumping rates can be achieved to depths of 45 m, and depth range can be extended through the use of an auxiliary power source.	
· These pumps are easy to operate, clean, and maintain in the field, and replacement parts are inexpensive.	
· In comparison to other pumps offering the same performance, these pumps are inexpensive to purchase and operate.	

Table 5.2C (con't)

Advantages	Disadvantages
Helical Rotor Electric Submersible Pump	
· This pump is portable and relatively easy to transport in the field to remote locations. · This pump is well-suited for use in wells of 5 cm (2-in.) inside diameter. · Relatively high pumping rates are possible with currently available units, thus well purging is possible. · This pump has been specifically designed for monitoring groundwater contamination; therefore, it is constructed of inert or nearly inert materials.	· The currently available pump unit is limited to 40 m of pumping lift. · High pumping rates with this pump lead to creation of turbulence, which may cause alteration of sample chemistry. · Thorough cleaning and repair in the field may be difficult because the pump is moderately difficult to dissemble. · Water with high suspended solids content can cause aeration problems. · The currently available model is expensive in comparison to other devices offering comparable performance. · The pump must be cycled on/off approximately every 20 minutes to avoid overheating of the motor. · The flow rate cannot be controlled, so the pump may not be suitable for taking samples for analysis of chemically sensitive parameters.

Table 5.2C (con't)

Advantages	Disadvantages
Gas-Operated Double-Acting Piston Pump	
· Because the sample is isolated from the driving gas, no aeration of the sample occurs.	· Piston pumps are relatively expensive in comparison to other sampling devices.
· The pump provides a continuous sample over extended periods of time.	· The pump is not highly portable - it must be vehicle mounted.
· This pump is relatively easy to operate and is easy to disassemble for cleaning and maintenance, though some maintenance problems (i.e., with the pump motor or valving mechanism) cannot generally be solved in the field.	· Unless the pump intake is filtered, particulate matter may damage the pump's intricate valving mechanism.
· Models of this pump are available for wells of 13.2 cm (¼ in.) inside diameter and for well of 5 cm (2 in.) or greater inside diameter.	· The pump's intricate valving mechanism may cause a series of pressure drops in the sample, leading to sample degassing and pH changes.
· The pump uses gas economically.	· Fixed-length tubing bundles may be inconvenient for shallow, low-yield monitoring wells.
· Pumping lifts of more than 150 m can be overcome with this pump.	· The tubing bundles may be difficult to clean adequately to avoid cross contamination.
· Flow rate of the pump can be easily controlled by varying the driving gas pressure on the pump.	
· The pump can be made of inert or nearly inert materials.	
· The moderately high pumping rate at great depths allows for collection of large volumes of sample in a relatively short time.	

Table 5.2C (con't)

Advantages	Disadvantages
Inertial Pumps	
· Very durable and can be constructed of chemically inert materials.	· maximum operating depth is determined by the limits of the actuator (i.e. approximately 90 m)
· Mechanically very simple; only one moving part.	· fine silts may clog the footvalve; however cleaning can be conducted very easily.
· Very simple to operate. They can be pumped by hand or with either an electrical or gas-powered actuator.	· turbulence and aeration may occur if sampling is conducted at the surface of the water column.
· Very inexpensive, thus allowing for dedicated well installation.	· applications using deep lifts or large purges may require either a mechanical, electrical or gas-powered actuator.
· Require no power source unless electric or gas-powered actuators are used.	
· Pumping and flow rates are controllable (0 to 15 L/min) and provide nearly continuous flow.	
· Can be used in wells as small as 1.25 cm (1/2") diameter.	
· Samples can be collected at discreet intervals and at any depth.	
· Do not require priming and are not restricted to limits of suction lift.	
· Can be used as zero-purge pumps (i.e. low flow pumping systems)	

Source:Modified from Nielsen and Yeates, 1985

Table 5.2D: Required Containers, Preservation Techniques, and Maximum Holding Times for Water Samples

Parameter	Container[1]	Preservative[2,3]	Maximum Holding Time[4]
Bacterial Tests			
Coliform, fecal and total	Sterile P, PET, G	Cool, 4^0 C 0.01 % $Na_2S_2O_3$ Pre-charged container	30 hours
Fecal streptococci	Sterile P, PET, G	Cool, 4^0 C 0.01 % $Na_2S_2O_3$ Pre-charged container	30 hours
Water Chemistry and Metals Tests			
Acidity	PET, G	None	14 days
Alkalinity	PET, G	None	14 days
Ammonia, total	PET, G	None	7 days
		H_2SO_4 to pH between 1.5 and 2.0	30 days
Biochemical oxygen demand, carbonaceous (CBOD)	PET, G	Add inhibitor: ATU or TCMP	7 days[5]
Biochemical oxygen demand (BOD)	PET, G	None	7 days[5]
Bromide	PET, G	None	28 days
Chemical oxygen demand (COD)	PET, G	None	7 days
		H_2SO_4 to pH between 1.5 and 2.0	30 days
Chloride	PET, G	None	30 days
Chlorine, residual	PET, G	None	Analyze Immediately[6]
Colour	PET, G	None	48 hours
Cyanide, total and amenable to chlorination	PET, G[7]	NaOH to pH> 12	14 days
Fluoride	PET, G	None	30 days
Hardness	PET, G	None	14 days
		HNO_3 to pH between 1.5 and 2.0	30 days
Hydrogen ion (pH)	PET, G	None	14 days
Total Kjeldahl nitrogen	PET, G	None	7 days
		H_2SO_4 to pH between 1.5 and 2.0	30 days

Table 5.2D (cont'd.)

Parameter	Container[1]	Preservative[2,3]	Maximum Holding Time[4]
Chromium (hexavelant - Cr^{6+})	G, T, with plastic-lined cap	None	5 days
Mercury (Hg)	G, T, with plastic-lined cap	1-2ml HNO_3 per 250 mls of sample followed by minimum 0.5 ml $K_2Cr_2O_7$ to a lasting yellow	7 days
Total metals (excluding Hg, Cr^{+6})	PET, G, with plastic-lined cap	HNO_3 (containing < 1mg/L of total metals) to pH between 1.5 and 2.0	60 days
Nitrate	PET, G	None	7 days
Nitrite	PET, G	None	7 days
Nitrate plus nitrite	PET, G[7]	None	7 days
		H_2SO_4 to pH between 1.5 and 2.0	30 days
Solvent extractable ("Oil & Grease")	G, Teflon- or foil-lined cap	None	7 days
Total organic carbon (TOC)	PET, G	None	7 days
		H_2SO_4 to pH between 1.5 and 2.0	30 days
Orthophosphate	PET, G	None	7 days
Oxygen, dissolved, Winkler probe	G only with glass stopper	None	Analyze Immediately
Phenolics (4APP)	G only, Phenol-free cap	H_2SO_4 to pH between 1.5 and 2.0	30 days
Total phosphorous	PET, G	None	7 days
		H_2SO_4 to pH between 1.5 and 2.0	30 days
Total suspended solids (TSS)	PET, G	None	14 days
Volatile suspended solids (VSS)	PET, G	None	14 days
Solids, dissolved	PET, G	None	14 days
Solids, total	PET, G	None	14 days
Specific conductance	PET, G	None	14 days
Sulphide	PET, G	0.5 ml 2N zinc acetate per 250 ml sample, followed by drop-wise addition 5% Na_2CO_3 to pH 10	14 days
Turbidity	PET, G	None	48 hours
Anions (Fluoride, chloride, sulphate)	PET, G[7]	None	30 days

Table 5.2D (cont'd.)

Parameter	Container[1]	Preservative[2,3]	Maximum Holding Time[4]
Organic Tests			
Volatiles, halogenated	G with teflon-lined cap, 40 ml EPA vial	None Allow no headspace.	14 days
		If chlorine present, 80 mg $Na_2S_2O_3$ per 1L, store in dark Allow no headspace.	14 days
Volatiles, non-halogenated	G with teflon-lined cap, 40 ml EPA vial	None Allow no headspace.	14 days
		If chlorine present, 80 mg $Na_2S_2O_3$ per 1L, store in dark Allow no headspace.	14 days
Volatiles, water soluble (Acrolein, Acrylonitrile)	G with teflon-lined cap, 40 ml EPA vial	None Allow no headspace.	14 days
		If chlorine present, 80 mg $Na_2S_2O_3$ per 1L, store in dark Allow no headspace.	14 days
Extractable, base/ neutral (includes PAH)	G, amber with teflon-lined cap	None	30 days[8]
Extractable, acid (phenolics)	G, amber with teflon-lined cap	None	30 days[8]
Extractable, neutral chlorinated	G, amber with teflon-lined cap	None	30 days[8]
Polychlorinated biphenyl (PCB)	G, amber with teflon-lined cap	None	30 days
Pesticides/herbicides	G, amber with teflon-lined cap	None	30 days[8]
Polynuclear aromatic hydrocarbons (PAH)	G, amber with teflon-lined cap	None	30 days
		If chlorine present, 80 mg $Na_2S_2O_3$ per 1L, store in dark.[9]	60 days
Adsorbable organic halide (AOX)	G, amber with teflon-lined cap	None	14 days
		Nitric acid to pH 2 and 1 ml of 0.1M sodium sulphite solution.	30 days
Chlorinated dibenzo-p-dioxins and furans (PCDD, PCDF)	G, amber with teflon-lined cap	None	30 days
Fatty and resin acids	G, amber with teflon-lined cap	None	7 days

[1] Polyethylene (P) or glass (G) or Polyethyleneterephthalate (PET) or Teflon (T). MOEE LSB requires the use of PET unless indicated otherwise.

[2] MOEE LSB requires unpreserved samples identified as "none" in this column. Alternate MOEE recommended preservation methods provided must be confirmed where other laboratories are involved.

[3] UNLESS OTHERWISE NOTED, ALL SAMPLES MUST BE MAINTAINED AT A TEMPERATURE BETWEEN JUST ABOVE THE FREEZING POINT OF THE SAMPLE AND 10^0 C AND BE PROTECTED FROM DIRECT SUNLIGHT DURING TRANSPORTATION AND STORAGE. Storage temperatures should be <4°C, but it is recognized that it is not always possible to strictly maintain this temperature.

[4] All samples should be analyzed as quickly as possible after sampling and transport to the laboratory. The maximum holding times listed are for samples maintained at the temperature indicated and differ for unpreserved and preserved samples.

[5] Samples must be transported to laboratory as soon as possible. Water samples have been stored for up to 4 days at 4°C with no appreciable loss of analyte.

[6] Analysis must be started as soon as possible. On-line or field testing is recommended where possible.

[7] Samples suspected of containing > 5% organic matter (solvents, hydrocarbons, etc.) must be stored in glass with a teflon-lined cap.

[8] Maximum storage time prior to initiation of analysis is for samples with first aliquot of extraction solvent added upon receipt at the laboratory. Otherwise analysis should be started within 7 days.

[9] The addition of preservative is required where PAH only is requested, or the levels of analyte are extremely low (e.g. parts per trillion analysis of surface or potable water).

5.3 Surface Water Sampling

Introduction

Sampling of surface waters for a site clean-up is necessary when a site assessment has indicated that there is a potential for contaminants to have adversely affected the quality of an on-site or nearby water body. The objective of the sampling will be to provide results that allow for the comparison of water quality immediately downstream from potential sources with that of upstream waters. For such comparisons to be made, replicate sampling is essential, and QC procedures that reduce the potential for contamination must be followed. This section provides information on sampling methods and procedures that should assist in producing high quality data. Most of the information was taken from the document "Protocol for the Sampling and Analysis of Industrial/Municipal Wastewater" (MOEE, 1993) and modified to be appropriate for sampling of surface waters for site clean-ups.

5.3.1 Sampling Methods

5.3.1.1 Manual Equipment

Most sampling requirements for surface water analysis can be fulfilled by manual sampling (i.e. grab sampling) using simple field equipment including: buckets, funnels, and suitable lengths of chain or dip poles. This equipment must conform to the same materials composition as the automated equipment outlined below (i.e. Teflon^{R}, stainless steel, glass, etc.). The equipment must be suited to the sampling and analysis being performed.

Manual sampling can also be conducted using an automated sampler in manual mode.

5.3.1.2 Automated Equipment

Where automated equipment is used, it is the user's responsibility to assure that the sampling equipment is clean, free from contamination and suited to the location, sampling and analysis needs. Generally, the cleaning and preparation of relocated equipment should include hot water, phosphate free detergent washing, hot and cold water rinsing, distilled water rinsing and finally, multiple rinses with the actual water being sampled.

Autosamplers must be mechanically and electrically suited to the environment in which they will serve and in consideration of safety and accessibility; be physically located to facilitate routine use, maintenance and inspection by field staff.

The three most important characteristics of automated sampling devices are:

1) materials composition;
2) temperature stability;
3) ability to obtain a representative sample.

1) Materials composition

All wettable surfaces that contact the water sample must be inert (i.e. must not contaminate, absorb nor desorb chemicals required to be analyzed in the water sample). This requirement can generally be met through consistent use of materials such as Teflon^{R}, glass, stainless steel and, where dictated by sampler design and function (i.e. peristaltic type pumps), short sections of surgical grade silicone rubber tubing. This type of tubing should be preferentially replaced by Teflon^{R} or other chemically inert materials as far as possible without impairing the performance of the sample device. Where surgical grade silicone rubber tubing is used, the total length should be kept to an absolute minimum and it is generally accepted that this should be less than 2 metres. Particular care must be taken to ensure that this tubing and all other wettable parts are cleaned or replaced at the first indication of discolouration or fouling.

These characteristics of sampler composition can be reviewed and adapted to suit the nature and sensitivity of the chemicals to be analyzed and the testing protocols to be used.

2) Temperature Stability

Another requirement for autosamplers is that they maintain the temperature of the sample between the freezing point of the sample and 10°C. This will require cooling and/or heating capabilities depending on location and time of year. This temperature maintenance is best monitored with a "min-max" thermometer and the readings documented in a sampler specific log book which should also incorporate repair, inspection, routine use, maintenance records, and be kept near the sampler.

3) Ability to Obtain a Representative Sample

Automated sampling devices can provide either:

1) a single large sample composite which can be further subdivided at the end of a predefined sampling period as suitable for the analysis to be performed or;
2) multiple individual composites which can be individually assigned to specific analytical test groups.

The latter capability can provide better flexibility and accommodate a wider range of analysis requirements by providing the option of individual container preservation - either pre-charged (phenolics and cyanide) or following the sampling period (metals, etc.), - and multiple composite samples for specialty testing needs (i.e. oil and grease analysis requires that the original container be submitted to the laboratory to be rinsed with extraction solvent).

The choice of autosampler design and capability will be dictated by site specific sampling and analysis requirements. It is, however, essential that the autosampler take its sample from a location in a stream that will provide a representative sample. This requirement will typically be met by sampling at a point of thorough mixing with no excessive turbulence (loss of volatile may occur) and at a point away from walls or surfaces of a pipe or channel that may cause insufficient mixing due to currents and eddies. The

sampling location may best be determined by practical tests to account for site-specific turbulence and mixing phenomena. Also, the sampler must maintain the sample integrity when transferring effluent from the stream to the sample container, in particular by maintaining adequate velocities in the transport system to exceed the scour and settling velocities of the constituents of interest.

If the stream contains volatile contaminants or constituents that can evaporate or be stripped, a representative sample is best obtained at a location of uniform concentration prior to the presence of turbulence.

5.3.2 Sample Types and Techniques

All samples obtained for analysis should be from a point in the stream that is representative of the whole stream composition. The volume of sample taken must be sufficient to allow for analysis of all required parameters plus associated quality control samples (i.e. field duplicate, laboratory replicate and spiked sample).

Grab

A grab sample is meant to represent the water stream at a given point in time as opposed to a composite sample which represents the wastewater stream over a longer time period (24 hours). Grab samples can be collected by using an automated sampling device in the manual mode, or by dipping an appropriate container, bucket bottle or vial, into the wastewater stream using an appropriate retrieval device such as a chain, rope or pole. Grab samples collected for analysis of compatible analytical test groups may be combined in a single large container and subdivided later, or they may be collected in several individual containers, each dedicated to a specific analysis. The following type of grab samples are defined. **Please note that these definitions have been changed from those in the MISA** document in order to emphasize the strong preference for Grab 1 in manual surface water sampling.

GRAB 1: The appropriate laboratory sample container is submerged in the water on a chain or pole until it is full; it is retrieved, preserved as necessary and capped.

GRAB 2: Water is collected in a bucket or other container and immediately transferred to the appropriate laboratory container(s), preserved as necessary and capped. The bucket must be thoroughly cleaned before it is used again.

GRAB 3: The wastewater is collected in a bucket as for GRAB 2 and the appropriate clean (outside as well) laboratory container (i.e. volatiles vial) is held at an angle and submerge into the liquid until it is full and air bubbles have been expelled, at which time it is carefully retrieved, preserved as necessary, and capped. Care must be taken to avoid sample contamination from the outside of the laboratory container or the retrieval device.

Samples for TPH, must be collected directly into the laboratory container, unless direct retrieval is impossible, to minimize unavoidable losses during transfer.

The sample size for a grab will be dependent on the testing that is required and the laboratory's sample size requirements for those tests.

The sampler should be careful to in no way contaminate or disturb the water upstream prior to sampling. This means that sampling within a stream should proceed from downstream locations to upstream locations.

The preferred method for sampling surface water bodies is to use a GRAB 1 method and slowly move the sample bottle through the depth profile of the water body as it is filling. When done properly, this method produces a sample that approximates the full depth profile of the constituent of interest in the water body.

Throughout all sample collection procedures, latex or PVC unpowdered gloves may be worn.

Composite Samples

When composite sampling is appropriate for a specific site, composite samples can be collected by either automated or manual methods.

Automated composite samples can be taken either proportional to the stream flow (in which case there must be flow sensing devices connected to the sampler) or on an equal volume/equal time basis. Both of these approaches require fully automated, programmable sampling devices.

Manual composite samples are typically taken on an equal volume/equal time basis but can be combined in proportion to flow once all subsamples have been collected. This basically represents a compositing of grab samples.

Composite samples are defined as follows:

AUTO 1 Automatic equipment collecting samples proportional to wastewater stream flow at time intervals of 30 minutes or less over a 24 hour period. The number and volume of samples is to be recorded.

MANUAL 1 A minimum of 8 grab samples taken at equally spaced time intervals over a 24 hour period (i.e. every 3 hours) combined in proportion to stream flow.

AUTO 2 Automatic equipment collecting samples of equal volume at equal time intervals of 15 minutes or less over a 24 hour period. The number of samples and the volume taken is to be recorded.

MANUAL 2 A minimum of 8 grab samples taken at equally spaced time intervals over a 24 hour period (i.e. every 3 hours) combined in equal volumes.

MANUAL 3 A minimum if 3 grab samples taken at time intervals of at least 6 hours over a 24 hour period. This technique is recommended for the sampling of volatiles, sulphide and TPH/solvent extractables.

AUTO 1 and MANUAL 1 are recommended techniques, while AUTO 2 and MANUAL 2 are acceptable alternatives, for all analyses except for volatiles, sulphide, and solvent extractables. For halogenated volatiles, the preferred method of collection is MANUAL 3, collected as GRAB 1. MANUAL 3 as GRAB 3 or GRAB 2 is an alternate method. For other volatile compounds, sulphide, and solvent extractables, the recommended methods are GRAB1, 2, or 3, or MANUAL 3.

Compositing Techniques

Where a sample is collected in a large container and requires analysis for several groups of compounds, the water must be allocated into the appropriate laboratory containers. Teflon^{R} tubing and gravity suction is recommended for transfer of the water to the individual laboratory container. A peristaltic pump may be used to transfer the aliquots into the appropriate laboratory containers, so long as the materials in contact with the sample conform to the requirements of Section 5.3.1.1 - Materials Composition. The sample may also be transferred to the individual laboratory container by pouring with extreme care to avoid turbulence. These aliquoting activities must be accompanied by continuous mixing of the composite sample by using a mechanical stirrer, manual swirling or other appropriate means.

Where grab samples are collected as part of a composite for volatiles and sulphide, each individual sample container must be submitted to the laboratory for analysis. The laboratory has the option of analyzing each sample and reporting the arithmetic means or of combining equal volumes of each grab and analyzing the resulting composite.

Where grab samples are collected as part of a composite for TPH analysis, each sample container must be submitted to the laboratory as this analysis includes solvent rinsing of each container.

Another option for tests such as TPH or sulphide is to collect three equal volumes of water into a single pre-graduated laboratory container, which, in the case of sulphide, has been pre-charged with preservative.

5.3.3 Preservation and Storage

Preservation

Some samples require preservation to ensure stability of the target compounds during

transportation and storage or to eliminate substances which may interfere with the analysis. In some cases preservation of the sample is optional, and if selected, will allow for a longer storage period before analysis must be initiated.

Preservation requirements and maximum storage times are outlined in Section 5.2.3 and in Table 5.2D (groundwater sampling) for each analysis.

Generally, samples requiring preservation must be preserved immediately upon collection, either at the end of the collection period for samples collected with an automatic sampling device, or after collection of each grab sample.

Where a composite sample is collected in a large container for analysis for several test groups, some of which require preservation, the samples must be preserved immediately following their transfer into laboratory containers.

Samples collected for cyanide and phenolics analysis using an automatic sampling device require separate containers and each must be pre-charged with the appropriate preservative as described in Section 5.2.

Where samples are to be preserved to a fixed set-point (pH, colour), care must be taken that the set point has been reached according to the best available detection technique applicable to the sampling location. This will include the use of: confined range pH paper; pocket/portable pH meters; standard colour comparison charts; etc. The use of these techniques and/or devices must not contaminate the sample.

Storage

All samples should be stored for as short a time interval as possible and under conditions that will minimize sample degradation.

Upon collection in the field, samples must be kept in the dark at temperatures above the freezing point of the water and under 10°C. It is recommended that sample temperatures should be brought down to below 4°C within 6 hours of collection. This means that automatic samplers must be refrigerated/heated and that samples must be transported in coolers and stored in refrigerators. Storage temperatures should be monitored, preferably with min-max thermometers, and documented in a log book.

The maximum storage times for each analytical test group are listed in Table 5.2D for each group of compounds to be analyzed. Storage time is defined as the time interval between the end of the sample collection period (typically 24 hours for composite samples) and the initiation of analysis.

Special Considerations and Precautions

- autosampler requirements

- separate containers for cyanide, phenolics, and TPH analyses

- Sample containers for cyanide and phenolics analysis must be precharged with preservative
- grab samples must be collected for volatile organic analysis
- caution on acid preservation of samples suspected of containing cyanide/sulphide and extreme ranges of pH in samples in general
- samples containing strong oxidizing agents (i.e. chlorine) should be neutralized as soon as possible after sample collection to prevent oxidation/degradation of vulnerable test groups

5.3.4 Field Quality Control

The principles and procedures outlined in Section 7 on Field Quality Assurance and Quality Control should be adhered to.

5.4 Sediment Sampling

Introduction

In order for a sediment survey to be of maximum benefit, it must meet all of the stated objectives of the survey. This requires that an adequate plan be prepared. This section offers suggestions on sediment survey designs, and, while not advocating that a particular methodology or protocol be followed, it is hoped that by avoiding common pitfalls in sampling design and implementation, many of the problems associated with poorly collected data can be overcome.

It is emphasized that the main guideline contain provisions for management decisions to be made both on the basis of the chemical quality of the sediments and on the basis of biological effects. Therefore, exceedences of both upstream sediment quality and criteria levels stated in the guideline provide a starting point for additional assessment of possible biological effects. In such cases, a clear definition of the potential biological effects is necessary before management decisions can be made. This section provides guidance on sampling for chemical quality assessment. For guidance on assessment of biological effects the reader is referred to the "Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario" (Persaud et. al., 1993) and its companion document "Sediment Assessment: A Guide to Study Design, Sampling, and Analysis and Laboratory Analysis" (Jaagumägi and Persaud, 1993) from which the current section is derived.

5.4.1 Design of Sediment Sampling Programs

5.4.1.1 Defining the Objectives of a Sediment Study

The reasons for undertaking the study and the questions to be answered form the basis of the study design. Therefore, objectives need to be clearly defined and described in detail before any survey plans are developed. When the objectives of the study are clearly laid out, they ensure that the essential work is carried out (according to budget allocations and schedule) and that non-essential activities are discarded.

Where the aim of the study is broad in scope, such as a complete environmental assessment of an area, the study should be divided into specific sub-objectives. There can be a number of these specific aims, such as comparison of concentrations among sites, mapping of contaminant distributions, and/or determination of biological effects. The study can then be divided into separate components that are designed to answer the specific questions. Ensuring that the specific concerns are addressed and that effort is not expended on those components that do not directly address the concerns is usually the most critical part of a sediment assessment study.

Identification of the specific aims of the study enables the proponent to select the most suitable tests and analyses and the best strategy for obtaining the samples. For site clean-ups where Ecological Risk Assessment is not indicated, these would be mostly chemical tests. In

most cases where a sediment clean-up action may be required, a detailed characterization of the area is in the best interests of the sponsoring agency/industry. In general, a clear delineation of the boundaries of a contaminated area could mean a significant reduction in the removal of excess (uncontaminated) material with corresponding cost savings in material removal (dredging) and disposal.

5.4.1.2 Designing a Sediment Survey

The development of a sediment sampling program would typically proceed through a number of steps.

i. *Review existing data*

Under this guideline, sediment sampling will only be conducted when the Phase 1 site assessment indicates the potential for sediment contamination. The initial step in designing a sampling program is to undertake a careful review of historical data. The purpose of this review is to characterize the existing sediments in terms of sediment type and potential contaminant concentrations, and to identify any gaps in the data. The proponent should be aware that the historical data may be incomplete, especially in the number of parameters measured, or out of date if the information is more than a couple of years old.

The data review should seek to identify all existing and historical contaminant sources to the area, such as industrial/municipal outfalls and urban runoff sources, in order to identify additional potential contaminants for which chemical analysis may be necessary.

Having collected all available data, the proponent should collate the information in order to identify any gaps. The filling of these gaps will assist in defining the sampling program to be undertaken.

Where historical information is not available, it is advisable to undertake a preliminary survey to assist in the planning of the detailed program.

At the conclusion of this stage there should be sufficient information to plan a sampling program which will generate the required information with minimal effort and time.

ii. *Define study area*

The study area should extend far enough spatially that it encompasses the entire zone of impact. A primary consideration is the need to delineate a study area large enough such that effects due to the source under investigation can be detected and that the severity of the effect can be determined relative to adjacent, unimpacted areas.

- historic or preliminary data should be used in delineating the study area and focusing the investigation.
- where previous information is not available, a preliminary study should be

considered in order to spatially define the study area.

- in lentic (standing) water (e.g., lakes), consideration should be given to wave action and current movements in order to project movement and dispersal of discharge from the source under investigation and thus help define the size of the study area.

- in lotic (flowing) water (e.g., rivers), consideration should be given to the flow dynamics of the watercourse and the nature of any discharges (i.e. do materials settle rapidly, or are they carried over long distances) when defining the study area. Preliminary studies or historical data can be of significant value, especially in identifying sources and extent of impact.

iii. *Determine most suitable study design.*

a) Sampling Strategies.

A number of strategies are available for designing sediment sampling programs. The choice of sampling strategy depends on the nature of the problem and the type of area being investigated. Baudo (1990) defines three primary sampling strategies that can be used to develop a suitable design:

1. Deterministic.

   This design is most often used where previous information is available. Under this approach, stations are located in relation to the specific concerns driving the investigation. The number of sampling stations is determined by how much detail is required on the site in order to address the concerns. Thus, for investigation of a near-shore discharge, for example, stations would be located on the basis of previous knowledge of sediment contaminant distributions or knowledge of plume movements from the discharge.

2. Stochastic.

   The stochastic system is most effective where data will be used for statistical analysis. The station locations are chosen by subdividing the area into equal segments and randomly selecting segments to be sampled (Baudo, 1990). This method can be applied to any type of study area, provided the size of the segments is appropriate to the study aims.

3. Regular Grid System

   Using this system the study area is divided into regularly spaced grids and the sample locations are selected either randomly (see 2. above) or deterministically (see 1. above) from the available grids. This is often the preferred method where little or no previous information is available or where a number of sources of contaminants may exist. In particular, this method is

commonly used where a map of sediment contamination is the desired product, since it provides uniform coverage of the study area.

For most assessment studies, some type of deterministic sampling method is used for the selection of sampling locations, either based on random selection or a regular grid system. Stratification of station locations, based on physical similarity of the sediments (determined through a preliminary survey), is often a necessary modification in random sampling designs, in order to achieve statistical comparability of results among stations. Since stratified random sampling is based on estimates of sampling error, this method requires prior information on the study area, either from previous sampling or from the literature, and can only be used where such information is available. Where review of the aims of the study has identified this method as the optimum survey design, a preliminary survey may be necessary before the final sampling program can be established.

In lentic (standing) water where the investigation is directed towards a specific point-source discharge, a deterministic sampling design is the most common. Using this design, sampling stations are located in a grid or radiating pattern around the source.

- The grid can be a regular grid based on lines intersecting at right angles, with sampling points located at the intersections. The spacing of the lines should be such that it provides adequate coverage of the area, with emphasis on areas of sediment accumulation and other known features.

- A radiating pattern can be used, with "spoke" lines radiating out from the source and intersecting arcs at right angles to these lines. The sampling locations are usually positioned at the intersections of these lines. The spacing of the lines should be based on existing knowledge of the site.

Sediment surveys in flowing water areas, such as a river, would require a grid system adapted to the longitudinal dimensions of the river.

- Where the investigation centres around a point source input of contaminants, a deterministic method is often used, with stations located at intervals downstream of the source. Station location would be based on suitable sediment types, with preference given to areas of similar substrate type in order to reduce variability and enhance comparability of results.

- Stations can be points in a river, or preferably, located on transects which span the river from bank to bank. If transects are used, a minimum of three points along the transect should be sampled (one sample in midstream, and one each on either side, the location of which would depend on the channel configuration at base-flow conditions).

b) Station locations should be considered in relation to other potential impacts.

The location of sampling stations in the study area should also take into account the location of existing water intakes and outfalls, the heterogeneity of the bottom materials, and

water movement (wave/current action).

- The distance between stations in a deterministic method, or the size of the sampling grid in a random or grid-based method depends on a number of factors, such as heterogeneity of the bottom sediments, the source(s) under investigation and the available funds for the sampling program.

- In areas of heterogeneous sediment, the number of sampling locations/stations should be larger than in areas of more homogeneous sediment in order to adequately define the sediment and the contaminant distribution.

c) Spacing of the stations or grids should be based upon the size of the study area.

- Where the area studied is large, the grid areas (usually squares or triangles) will also be large. The result is that the area of sediment each sample represents also becomes proportionally larger. This presents difficulties, since the larger the area each sample has to represent, the less representative of that area each sample becomes. The resolving power of studies based on large grids is usually low, and these studies are most effective when performed in an area of generally more or less uniform bottom characteristics. They would, for example, be suitable for the study of the profundal areas of large lakes where the physical characteristics of the area would not be expected to change over large areas.

d) The physical characteristics of the sediment can influence the number of stations and their locations since sediment type has been shown to significantly affect the distribution of contaminants. For assessment of chemical contaminants, sampling should concentrate in areas of fine-sediment accumulation. The use of a grid in sampling areas that are similar in physical characteristics (i.e., depth, sediment type) can result in the collection of a large number of samples where a few would suffice (Baudo, 1990).

- Sampling programs designed to assess the nature and extent of contaminants in sediments (from either point or non-point sources) should be directed towards sampling areas of fine sediment accumulation. Fine sediments often accumulate higher levels of contaminants than coarse sediments, since fine organic matter will preferentially bind many persistent organic compounds. Metals are also affected by organic matter through the formation of metal-organic matter complexes.

- In flowing water, preference should be given to areas of fine sediment accumulation, such as natural depressions in the bottom, pools, quiescent areas or artificial depositional areas such as occur behind dams.

- In a random sampling design, stratification based on particle size would be the most useful. Since stratification depends on preliminary information or existing studies, this technique can only be used where such information exists.

- Stratification on the basis of particle size may not be advantageous where the aim is to assess the sediment characteristics of a section of a waterbody or watercourse such as in sediment mapping studies.

- In areas of heterogeneous sediment, the number of stations required to adequately characterize the substrate will be higher than in areas of homogeneous sediment distribution.

For basin-wide or sediment mapping studies, where general assessment of sediment conditions within an area is the primary aim of the study, sampling is usually based on a pre-determined pattern and will often include areas of varying grain sizes.

- In these types of studies it is necessary to sample the existing bottom sediments throughout the area in order to properly characterize the sediments, usually in terms of the existing sediment types and their respective contaminant concentrations.

- The potential biological availability of contaminants from sediments of coarser size fractions (i.e. sands) low in organic matter is generally higher than from fine sediments and their assessment may be important in terms of determining potential remobilization of the contaminant. However, in most cases this sampling should be considered as additional sampling, and not done at the expense of sampling the fine-sediment.

- In flowing water situations, the stations could be arranged on a more regular grid pattern and sampling locations selected either through random selection or through the deterministic method. In such cases, preference should not be given to sampling any one sediment type, since the distribution of sediment types and their contaminant concentrations within the river is one of the aims of the study. However, such studies would usually require a larger number of samples in order to adequately characterize an area, since both coarse and fine grained sediments need to be characterized. In such cases, prior knowledge of the sediment physical characteristics would be necessary.

- Where sediment conditions would be expected to be relatively uniform over large areas, such as in large lake basin-wide studies, the number of sampling locations in the deep profundal areas could be reduced, with relatively large distances between sampling points.

- Where more heterogeneous conditions exist, such as in nearshore areas or in harbours and river mouths, the number of sampling points should be greater and the sampling points closer together.

- Prior knowledge of the sampling area can be a significant asset and can ultimately determine the success of the program.

e) In areas where the bottom characteristics are variable, the area may be subdivided into

smaller study units.

- Sampling in these smaller areas would be based on grids as well, but the grids should be smaller, such that each grid represents a small area of bottom. This will ensure a higher density of sampling within these areas. In nearshore areas where bottom characteristics can be highly changeable, some variant of stratified random sampling can be used.

f) A suitable control or controls must be located upstream of the study area or outside of the zone of impact. Stations do not have to be placed an equal distance apart and could, for example, be spaced further apart with increasing distance from the source. This would permit higher sampling density in those areas closer to the source, where the greatest impact would be expected. Sampling should be extended far enough from the source(s) that the final sample lies outside of the zone of impact.

g) The sampling design should consider data requirements for statistical analysis. Where such requirements exist, the design should be modified such that adequate information will be available to carry out the analysis.

- Combining different types of sampling grids usually limits the use of the data for routine statistical tests. However, techniques such as "kriging" are available for analyzing such information and are recommended where there is a mix of sampling or grid density. The larger grids can be subdivided into smaller grids, thereby increasing the sampling frequency within an area. Thus, where a harbour or river mouth is located within the larger study area, this area can be sampled at a density greater than the open (profundal) lake areas. Generally, a grid would be sampled in the centre of the grid, though any part of the area can be used as long as this is consistently followed throughout the study. For example, the intersections of the lines could form the station locations.

Many of the methods for determining sampling locations that have been described have depended on existing historical or preliminary data. Often, however, such data are not available and planning must proceed without the benefit of prior knowledge of the site. Under these circumstances the sampling design is usually based on a regularly spaced grid with station locations determined randomly or deterministically. Efforts should be made to sample as many stations as possible, since in most cases the survey will form the baseline study in that area. A large number of sampling points is also essential for any study where statistical analysis forms a part of the data analysis (e.g., trend analysis, GIS, etc).

h) Waterbody Dynamics

The density or spacing of the stations will also depend on the flow dynamics of the receiving water in relation to the discharge. A high volume discharge into an area with pronounced wave or current action, or to a large river with strong flow would carry a larger contaminant load for a greater distance from the source, resulting in a greater area to be sampled. In some cases, sampling may have to be carried out to the mouth of the river, since

this is the area where most of the fine sediment load (and associated contaminants) will be deposited.

- The importance of preliminary or historical information in the success of a study cannot be overstated.

i) Contaminant Characteristics

In planning the station locations, consideration should also be given to the type of contaminant(s) involved and the suspended and bed load of the river. Contaminants that sorb rapidly to suspended matter will be carried with this material, while contaminants that remain in solution for extended periods may only be of concern in the lake or other body of water into which the river drains. In standing water, such contaminants may be broadly dispersed throughout the waterbody. In either case, availability of contaminants to biota may be considerably enhanced.

j) Subsurface Sediment

One additional consideration, that will not apply to all types of studies, is determination of the depth to which samples should be taken. The accumulation of sediment over time can result in variations in contaminant concentrations within the subsurface sediment layers. In most sediment assessment studies, only surficial sediment characterization is of concern. However, where a historical record is required, especially where remediation is a concern, or where dredging is proposed, sampling may have to be undertaken to considerable depths.

- Depth of sampling is determined by the specific aims of the study and often these are related to assessment of the effects of historical sources of contaminants.
    - The depth of sampling should be based on an estimate of the yearly sedimentation within the area (harbours will naturally have a higher sedimentation rate than deep basins of large lakes in well forested watersheds) and the historical data available for the operation of any contaminant sources.

Sampling of surface and sub-surface sediments requires different sampling devices as well as different approaches to sampling design. A discussion of sampling devices for sediment studies is provided in Table 5.4A.

k) Number of Stations:

The number of stations necessary to adequately characterize sediments within a study area will vary according to the type of study and the aims of the study.

The number of samples required to obtain a statistically significant result has always been a difficult issue to address, since the distribution of contaminants in sediment is

essentially non-random. For statistical purposes, characterization of sediment quality at the P < 0.05 level can range into hundreds of samples, depending on the level of certainty desired. Dividing the study area into a number of sampling locations, and collecting replicate samples from each of these has been devised as a practical alternative to collecting a large number of samples at a single station (Baudo, 1990).

Baudo (1990) discusses methods to determine the statistically acceptable minimum number of stations for any sediment survey where data are available from previous studies. The procedures can be used to determine the number of stations necessary to derive an average value for an area, with a given statistical uncertainty.

The density of sampling will reflect both the needs of the project and the availability of resources. Thus the amount of detail needed will determine the number of stations.

In most sediment studies, the final aim is to compare sediment contaminant concentrations with the available guidelines.

- Where sediment contaminant assessment is the specific aim of the study, the number of replicate sediment samples should be set at a minimum of three (with the exception of analyses for dioxins and dibenzo-furans). The mean of the replicates is compared to the guidelines values.

- Between three and five replicate samples from each station are recommended in order to provide an estimate of the mean and standard deviation around the mean. However, it is recognized that this type of sampling can add significantly to the cost of a study, or alternatively, may lead to a reduction in the number of stations/locations sampled. Therefore, many studies rely on a single sediment sample per station, usually collected as a composite of a larger number of samples.

- Composite samples are obtained by collecting a number of replicates (usually 5) which are then combined and homogenized. A sample of the homogenate is collected for analysis.

- For most purposes this will be acceptable, though the sample will give only an average/mean value over that area and, while costs are minimized, the method does entail a loss of information such as the range of contaminant concentrations encountered.

- In cases where remedial action may be considered, or where severe contamination is expected, composite samples are not recommended. In such cases, a larger number of replicates should be considered in order to more clearly and accurately define the nature of the area.

5.4.1.3 Spills Assessment and Clean-up

The design of a sediment sampling program for the assessment of a spill requires some

special considerations. Without exception, the aims of such studies are to assess the extent of the contamination and determine the immediate need for remediation. In most cases, clean-up will consist of some type of dredging.

The principal aim is to rapidly assess the extent of the spill. This can be done visually by divers, where it is safe to do so. It is also necessary to assess the depth of the contaminated material, which will require sampling and chemical analysis. Since visual inspection may not necessarily define the extent of the spill, the final sampling area should be at least one third larger than the estimated area of the spill. In any event, it will be necessary to determine ambient concentrations of contaminants outside the spill zone, since these will determine the clean-up criteria.

1. Establish boundary of spill by initial visual survey, if safe to do so. Otherwise, conduct visual survey from boat or sampling platform, visually inspecting sediments, until an approximate boundary can be established.

2. Assess existing physical factors such as current, slope, wave action, that may influence movement of spilled material.

3. Assess the nature of the material spilled (physical and chemical properties)

4. On the basis of 1 to 3 above, determine the extent of the sampling area. The final sampling area should be 1/3rd larger than this area since in all clean-up operations both the extent of the spill and local ambient levels need to be defined.

5. Select most appropriate sampling device. In nearly all cases some cores will always have to be taken since depth characterization will be required to determine proper clean-up depth.

6. Define parameters for analysis. This will be determined on the basis of the material spilled.

5.4.2 Sediment Sampling Methods

5.4.2.1 Sampling Devices

Over the year a variety of sampling devices have been developed for sampling sediment and sediment-dwelling organisms. These devices fall into two main groups: grab samplers and core samplers.

Grab samplers are jaw-like devices designed to collect surficial sediments by scooping out a defined area of the sediment surface. The depth of collection is limited by the height of the sampler (i.e., the volume) and the nature of the sediment material. Their ability to collect a sample is a function of the degree of penetration (firmness of the sediment relative to the weight of the sampler), angle of penetration, depth of water, and lateral motion of the boat or sampling platform during collection. Unless sealed at the top, there is also a tendency for

"washout" of fine-grained materials during retrieval. Two of the most commonly used grab samplers are the Shipek and the Ponar. Descriptions of these devices are included in Table 5.4

Core samplers are usually tube-shaped devices which can penetrate the sediment by gravity (freefall), vibration or hydraulic pressure (water or oil). These collect sediment to a much greater depth than grab samplers (depending on the length of the collection tube fitted to the sampler). Table 5.4A, taken from Sly (1969), describes the various types of samplers, both corers and grabs, and their advantages and limitations.

The distribution of contaminants in sediments varies both horizontally and vertically. Horizontal variation can be assessed by the collection of samples from selected sites throughout the project area. Typically, the concentration of contaminants also varies with depth in sediments. If information on variability with depth is required, it is recommended that sediment samples be collected using either a coring device from a boat or having a diver collect a core. A grab sampler is recommended if information on surficial sediment only is required.

The typical coring device is a length of pipe with a weighted head of 50 to 200 kg. Inside is the plastic liner (polybutylacrylic plastic is recommended). At one end is a metal core cutter which assists the coring device to penetrate the sediment and a core catcher to retain the sediment in the liner. At the top end is a ball-valve or piston which retains the sediment in the liner when the device is pulled back out of the sediment.

There are three major drawbacks to the gravity core sampler:

1. There is a "shock wave" ahead of the sampler before it penetrates the sediment. This may displace the very unconsolidated top layer of sediment;

2. The gravity action tends to compress the sediment during penetration, thereby compressing the vertical profile of the contaminants (Baxter *et al.*, 1981); and

3. The use of a small sampling boat necessitates the use of a small core sampler with a small head weight. The small barrel diameter of the sampler can cause gross disturbance of the sediment profile during penetration, potentially destroying the vertical profile of the contaminants. The small weight may lead to insufficient penetration.

A diver-collected core is preferred over a core collected by a free-falling coring device. The diver is able to carefully insert the liner in the sediment, minimizing the disturbance of the surficial sediment, virtually eliminating the compression problem and is able to use a relatively wide diameter liner. The use of a diver also permits an observation of the general nature of the bottom and the presence of aquatic biota. A limitation of the diver-collected core is that the retained length is typically less than 1 m.

The core and grab samplers described above are best used in fine sands or muds. Collection of grabs of coarse sand or cobble requires a large and adequately weighted grab (larger than 0.5 sq m capacity). A vibra-corer is required to collect a core in coarse or compacted sand. This device is similar to the gravity corer, but a vibration source is attached

which vibrates the barrel down into the sand. Such a corer may require a specialized sampling boat, due to the weight of the equipment and the power requirements.

Final selection of the sampling device will depend on the characteristics of the site and the objectives of the study. Where stratification of the sediment is suspected or is a concern, a coring device would be the preferred choice. Where sediment layers are homogeneous, or the vertical profile of sediment concentrations is not important to the aims of the study, a grab sampler may be more effective/efficient (in terms of costs).

Table 5.4A: Operational Evaluation of Sediment Sampling Devices
(from Sly, 1969)

GRAB SAMPLERS	Characteristics
Ponar Grab	An excellent general purpose bottom sampler.. It can also obtain samples with little or no disturbance and with the protecting screens removed or folded back, direct access can be had to the sediment surface of the sample. Such access to undisturbed samples makes it suitable for geochemical, sedimentological, biological and structural studies. Because of the large sample volume and its relatively undisturbed state, this sampler is very suitable for population studies of the bottom sediment fauna.
Shipek Grab	An excellent general purpose sampler, though perhaps a little heavy for small boat operation. This sampler is capable of working with almost equal success on all types of bottom materials. It provides a sample even less disturbed than the Ponar, making it the most suitable sampler (under test) for detailed geological studies of the sediment surface. The sampler volume is significantly less than that of the Ponar, and the quantity of material sampled at maximum cutting depth is also less than the Ponar. These two points may, therefore, favour the Ponar for certain biological (population) studies. On the other hand, the rapid rotation of the Shipek bucket, as opposed to the much slower closure of the Ponar's jaws, may make it more suitable for sampling sediment containing a significant population of non-sessile forms.

Grab Trigger System Reliability

Ponar Grab	Good. Tends to be a little over-sensitive on gravel bottoms.
Shipek Grab	Good, though some slight settlement may occur before triggering on very soft materials. Sampler may fail to trigger when lowered gently on soft bottoms. By lifting and dropping the trigger weight a few centimetres after bottom contact, abortive casts may be avoided. The slight movement of the inertial trigger weight has no other affect on the sampler.

Grab Jaw Shape, Design and Cut

Ponar Grab	Excellent. Jaw shape exactly follows arc of cut and almost no sample displacement occurs.
Shipek Grab	Excellent. As for Ponar. In addition, the rotation of the bucket is extremely rapid. In most cases, the rotational shear is far greater than the sediment shear strength, thus the cutting action is very clean (producing minimal disturbance), particularly in soft clays, muds, silts and sands.

Preservation and Protection from Washout in Grabs

Ponar Grab	Good, except when the sampler is used in very coarse or shelly sediment. Under these conditions, material may be trapped between the jaws, preventing their closure. In this case, washout can be severe. The jaws are designed to slightly overlap one another, thus, a slight imperfection in closure can be tolerated. In addition to the overlap jaws, this sampler has a pair of metal side plates, mounted close to the moving side faces of the jaws. These plates further reduce the possibility of washout.
Shipek Grab	Excellent. The great advantage of the Shipek, over other samplers, is that the bucket closes with its separation plane aligned in the horizontal rather than in the vertical. Good samples can be retrieved even when bucket closure is prevented by pebbles or similar material, even 2 to 5 cm across. With the bucket properly rotated, washout is completely avoided.

Stability

Ponar Grab	Very good. This is a heavy sampler with a wide base line (when the jaws are open). It maintains a near vertical descent

	under all conditions. Because of its weight and wide baseline, this grab has a good vertical descent under most conditions and has a stable stance on the bottom. The presence of the fixed side plates prevents the grab from falling over after jaw closure and helps in preserving a near perfect bottom sample.
Shipek Grab	Excellent. Despite the large size of this Grab sampler, its weight ensures a near perfect vertical descent even under conditions of rapid drift or fast water flow. The sampler is also very stable even on bottom slopes 20 degrees or more. This stability ensures the minimum possible disturbance of the sample material.

CORE SAMPLERS

Characteristics

Benthos Gravity Corer	Cores of 3 m or less in soft clays, muds or sandy silts, particularly suitable for studies of the sediment/water interface, for studies on depositional sediment structures.
Alpine Gravity Corer	Cores of 2 m or less in almost all sediment types. The rugged nature of his corer lends itself to general usage. For studies involving sediment structure or large volumes of material, the corer is unsuitable; for studies of a pilot nature, or to prove the suitability of an area for piston coring, this gravity corer is excellent.
Phleger Corer	Cores of 0.5 m or less, in almost all sediment types, particularly suited to bottom materials containing a high percentage of fibrous organic material. The low cutter angle, the narrow wall thickness and high point loading, and the extremely sharp cutter, make it very suitable for sampling shallow lacustrine and estuarine deposits, marsh deposits and thin peat beds.

5.4.2.3 Sample Collection

Due to design characteristics, coring devices generally provide the most representative samples with the least bias, at least in soft substrates. Grab samplers are affected by sediment

texture and the size of the sample will depend on how deep the sampler sinks into the sediments and on whether the sampler will rise upon closure of the jaws. Thus, while the surface area to be sampled will be the same, the samplers do not always sample the same volume of sediment. With gravity coring devices a similar problem can be encountered where the sampler may sink down into the sediment. Core samples are directly comparable only if the volume of the sample can be closely controlled to ensure a similar depth is collected each time. However, grab samples are more cost effective since fewer samples are required to sample the same area of sediment.

In soft sediments, sampling with either corers or grabs requires that the sampler be lowered slowly to minimize the creation of shock waves at the front of the sampler that may disturb and resuspend sediment material and attached organisms, thus biasing the results.

The collection of samples from firm substrates and hard-bottomed areas presents special problems. In deeper waters, firm substrates such as gravel or cobble often require specialized equipment (suction samplers) which generally must be operated by a diver. In shallow waters these can be collected with simple devices such as surber samplers. The mixing of soft and hard substrate areas within a study area can also lead to considerable bias due to the volume of sample collected.

5.4.3 Field Record Keeping

Positioning

Sample site locations should be determined as accurately as possible in the field and precisely located on a map. Positioning is especially important if the sites are to be re-sampled at a later date. Accurate positioning is also important for later analysis of the data using Geographical Information Systems, and where possible should include either geographical coordinates or UTM coordinates.

The sample sites can be determined using landmarks, actual measurements, distance estimator or electronic positioning equipment. When available, electronic positioning equipment (side-scan sonar, Loran-C) provides the most accurate result.

For certain types of studies, such as those for dredging projects, submission of a detailed plan of the project site delineating the site boundaries and the location of the sample sites, is a very important feature of the application for environmental review. A chart scale of 1:500 or 1:1,000 is recommended.

Field Notes

The information gathered for sediment evaluation should include field notes covering the following points:

- current speed near bottom
- weather conditions;

- time and date of collection;
- positioning information;
- type of sampler used;
- name of sampling personnel;
- notation of odd or unusual events which occurred during sampling (e.g., "corer returned only a few rocks");
- field description of samples:
  - odour,
  - approximate particle size,
  - colour,
  - presence of non-decomposed organics (e.g., wood fibres),
  - presence of oil and grease,
  - presence of distinct layering as given by changes in colour or particle size,
  - presence and type (to broad groupings) of aquatic biota, and
  - length of retained core;
- brief description of handling procedures and types of containers used;
- notation where there was a deviation from standard handling and splitting procedures; and
- laboratory to which samples were delivered and the date of delivery.

If the proponent is routinely having samples collected, a standardized form covering the field information is recommended.

Physical Analysis

Before a sample is mixed and split in the field, the odour and colour should be noted and the pH and redox potential measured. Odour can be divided into four categories:

- Odourless
- Chemical
  - chlorine
  - petroleum
  - medicinal - phenol, iodine
  - sulphurous
- Decaying Organic
  - manure
  - sewage
- Natural
  - earthy
  - peat
  - grassy
  - mouldy

Colour can be best determined by comparison of the sediment to the Munson colour code

system. If that is not available, each colour zone or depth of core should be described. Colours will range from reddish-brown to jet black.

The pH and redox conditions should be measured with appropriate electrodes which have been properly calibrated. The electrodes should be rinsed with clean water between measurements and stored in appropriate containers. Accuracy of measurement should be ± 0.1 pH units; ± 10 mv for redox potential.

5.4.4 Field Storage and Handling

Grab Samples

If redox and pH measurements are required, then the probes should be inserted into the sediments (3-5 cm), as soon as the grab is collected. If possible, the probes should be inserted and samples removed through top-access doors rather than transferring (and thereby mixing) the sample into a pan. Observations should also be made at this time: presence of oxidized surface layer, colour and smell of underlayer, approximate particle size description and presence of obvious oil or grease or non-decomposed organics (e.g., wood fibres).

The top 3-5 cm of the grab sample should be transferred into a clean pan and thoroughly mixed using a large, clean teflon or ceramic spoon. Subsamples should be handled as follows:

1. For metals/particle size/carbon/ phosphorus/total Kjeldahl nitrogen/loss on ignition, place in clean plastic or glass containers; and

2. For trace organics/TPH, place in clean solvent-rinsed glass bottles with clean aluminum foil cover caps. Amber-coloured bottles are preferred.

The amount of sediment required for analyses should be determined in consultation with the analytical laboratory. The samples must be kept at 4°C and out of sunlight. Samples should be shipped to the laboratory as soon as possible after collection. Sample containers should be carefully labelled with indelible ink pens. Labels should contain the following information:

- date and time of collection,
- identification of collector, and
- site identification (including harbour name).

This information should correspond to information recorded in the field notes.

Cores

With the bottom end of the liner securely capped, the excess water should be carefully decanted or siphoned. The core may need to stand for some time to permit settling out of disturbed material before decanting.

The length of retained material should be measured in centimetres. Excess core liner should be cut off and the top of the liner capped. The core should be retained upright and carefully labelled. It is suggested that the label be placed only on the top end of the liner, to ensure that the core is not inadvertently turned over during transit or storage. The core should be handled in such a way as to prevent "sloshing" of the material.

As with the grab samples, the core samples should be stored at 4°C. As the cores may be long and cumbersome, it may be convenient to split the cores in the field. (This is best done on shore). Before extrusion, the core should be examined and the depths where redox discontinuities occur should be noted. The cores should be extruded from the bottom end (the firmer end). The core sample may be sectioned in one of two ways. The first way is to section the sample according to the different layers if the colours are obvious. Otherwise, samples may be sectioned into top, middle and bottom sections or sectioned at regular intervals (e.g., 5 cm). The actual amount should be determined in consultation with the analytical laboratory. Each section should then be treated as a separate sample and handled as described above. This will include measurements of pH and redox, noting colour, odour, redox discontinuities, approximate particle size and presence of oil or organic matter; non-decomposed organics etc.

Archive and Duplicate Samples

Sediments may be heterogenous and therefore must be thoroughly mixed before they are subsampled. Each container should be mixed and sub-samples taken for the required analysis. Remaining material should be combined into one container and this preserved frozen as an archive sample. This should be retained for at least one year or until the dredging operation or study is completed.

The purpose of the archive sample is to permit subsequent re-analysis for a particular constituent or external audit analysis. For field and laboratory quality control and quality assurance, the following duplicates must be taken. For example, if 5 samples are to be taken, 1 additional sample is to be taken as a field duplicate. The laboratory views these as 6 unknowns and therefore there would be 6 laboratory samples and 1 laboratory duplicate for a total of 7 samples for analysis.

5.4.5 Field Quality Assurance and Quality Control

The principles and procedures outlined in Section 7 on Field Quality Assurance and Quality Control should be adhered to.

5.5 Air Sampling

5.5.1 Principles of Air Sampling For Site Clean-ups

Ambient air monitoring during a site clean-up is conducted in order to detect airborne contaminants which may harm human beings, animals or the surrounding environment, and to monitor in a timely way so that appropriate control action can be taken. Not every decommissioning/site clean-up will require ambient air monitoring. Local MOEE staff can advise if it is required. In some cases, Ministry of Labour monitoring for worker protection could be sufficient.

The following general principles should govern the design of the sampling program, where required.

- Monitoring should be performed for those contaminants which are known to be present on the site or which could reasonably be expected to be emitted from the site.

- Samplers should be sited close to the fence line or property boundary upwind and downwind of the site, according to the prevailing wind direction. Normally, a minimum of four sampling sites will be employed.

The sampling program will normally consist of three phases; 1) pre-operational, 2) operational and 3) post-operational.

1) The pre-operational sampling is performed to determine the background levels of site contaminants in the area. Sampling frequency can be every sixth day for four weeks, every third day for two weeks, or some similar frequency. Sampling should not take place on forecast rain days.

2) The operational sampling program during actual site decommissioning should begin with frequent sampling for toxic contaminants and with rapid turnaround time for analysis. If off-site levels of contaminants meet standards, then the frequency can be reduced to once every three or six days depending on the length of the project. Timing and frequency of sampling should address site activities.

   In addition, ongoing real time monitoring should take place for toxic contaminants or a surrogate (e.g., total hydrocarbons using a photoionization detector). These measurements will allow control of site activities if there are short term problems.

3) After site clean-up is complete, there should be a short period of post operational monitoring to ensure that there is no ongoing threat to the neighbourhood. This may be waived if no impacts were detected during operational monitoring.

The main types of sampling are listed below, and detailed sampling guidance is provided in Section 5.5.2.

1. Particulate sampling - this can be performed using high volume samplers as well as

dustfall jars. If appropriate, the samples can be analyzed for metals as well as total dust. If work on the site is only performed during the daylight hours, then the samplers should only operate for 8 - 12 hours during the work day and the measured value should be compared to a pro-rated objective rather than the 24 hour objective.

2. Semi volatile sampling - this is performed using modified high volume samplers with adsorbent backup to monitor for PAHs, pesticides, etc.

3. Volatile organic compound sampling - compound specific monitoring is performed using adsorbent tubes with subsequent analysis at the laboratory. Half-hour exposures may be necessary. Real time monitoring should also be performed at the site using non-specific hydrocarbon detectors so as to control site activities, in case foam blanketing or other control measures are required.

All exceedences must be reported to the MOEE immediately.

5.5.2 Sampling Methods

5.5.2.1 Particulate Sampling

Particulate sampling may be performed using high volume (HiVol) samplers, dustfall jars, or samplers that preferentially collect particulate of a specified aerodynamic diameter such as HiVol samplers with size selective heads or dichotomous samplers. The type of sampler selected should reflect the end use of the data collected. If particulate sampling is being carried out mainly to monitor for soiling then HiVol samplers and dustfall jars are appropriate. If inhalation is the main concern, rather than soiling, a size selective particulate sampler should be used.

Dustfall jars are open jars placed at the sampling site for a specified duration. The collected dust is then weighed to determine particulate concentration. The dust may also be analyzed for metals if necessary.

A HiVol sampler consists of a vacuum motor drawing air through a particulate filter at a constant rate. The filter is conditioned at known relative humidity and temperature and then weighed before use. After the sample has been collected, the filter is re-conditioned at the same relative humidity and temperature and is then re-weighed. The total particulate mass collected divided by the air volume sampled yields particulate concentration in micrograms per cubic metre ($\mu g/m^3$).

There are two main types of size selective particulate sampler. One type consists of a HiVol sampler fitted with a special head. The operating flow rate of the HiVol sampler (40 cubic feet per minute) and the design of the special head combine to restrict particulate sampled to the respirable size range (0-10 μm). The other main type of size selective sampler is a dichotomous sampler. This sampler operates at a lower flow rate than a HiVol sampler. It samples particulate in two size fractions: < 2.5 μm and 2.5-10 μm. As with the size selective HiVol, the flow rate and head design restrict sampling to particulate < 10 μm.

The internal configuration of the sampler then separates the particulate into the two size fractions mentioned. The smaller size fraction is of concern as these particles may penetrate deep into the lung.

For HiVol and dichotomous samplers, special care must be taken when conditioning and weighing filters both before sampling and after the sample is collected. HiVol filters may stick to the filter hold-down frame on the sampler. If part of the filter is lost in this manner the calculated particulate concentration will be in error. Care must also be taken so that no particulate is lost off the filter when the sample is changed. Filters for dichotomous samplers are much smaller than those used in HiVol sampling. Weight differences between clean and loaded filters are typically a few thousandths of a gram, and neutralizing any static charge on the particulate becomes important. This is accomplished with a radioactive source, such as Polonium 210, in the weighing chamber.

The size selective properties of both types of particulate sampler are sensitive to variations in sampling flow rate. It is important to ensure that the samplers operate within the sample flow rate parameters specified by the manufacturer.

5.5.2.2 Semi-Volatile Organic Compounds

Semi-volatile organic compounds (SVOC) are chemicals with vapour pressures in the range 10^{-2} to 10^{-8} kPa. These chemicals may be distributed between the vapour and particle-associated phases making air sampling more complicated than for particulates or for volatile compounds which usually exist in the atmosphere only in the vapour phase. The sampling methods described here are suitable for polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), pesticides, and polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF).

Sampling for SVOCs is accomplished using a high-volume sampler modified to accept a vapour trap downstream from the particulate filter. A vacuum pump is used to draw air through the filter and sorbent. Sampling flow rates vary between about 15 cubic feet per minute (cfm) and 40 cfm depending upon the type of sorbent used (which influences air flow restriction) and whether a flow controller is used or the sampler is operated at full line voltage. Sampled air volumes are obtained from the sampling rate set by the flow controller and the elapsed sampling time or from an in-line rotary vane or dry gas meter.

A teflon-coated glass fibre filter is used to trap the particle bound compounds. These filters have an efficiency > 99.9% for particles ≥ 0.30 μm at the operating face velocity of the sampler (Liu, et al., 1983).

The most commonly used sorbents for vapour phase compounds are XAD-2 resin and polyurethane foam (PUF). Discussions of both are adapted from Hunt (1986).

XAD-2 RESIN

Amberlite® XAD resins are synthetic adsorbents. Analyses of XAD-2 have shown

consistent and significant contamination due to a variety of aromatic hydrocarbons. The extractable contaminants are either residuals from the resin manufacturing process (e.g. starting materials or secondary by-products) or artifacts from the degradation of the polymer itself during storage and handling following the actual manufacturing process. Regardless of where the contamination comes from, XAD resins require rigorous clean-up prior to use. The most widely accepted clean-up procedures employ sequential solvent extraction in a soxhlet apparatus. Continuous extraction using a sequence of water, methanol, and methylene chloride will virtually eliminate detectable organic extractables from the sorbent matrix. Contamination appears to be qualitatively consistent from lot to lot possibly due to the patented process employed by Rohm and Haas in the manufacture of the Amberlite® resin product line.

Polyurethane Foam

Unlike the XAD resins, polyurethane foam (PUF) is synthesized via any one of a number of patented processes. The most common methods use organic isocyanates (aliphatic or aromatic) and a polyol as starting materials. Also, a number of chemical additives are introduced during the process to impart specific chemical or physical properties to the final foam product. For example, fire retardant properties are obtained by adding high molecular weight halogenated organics.

The quality of PUF varies markedly from supplier to supplier and from manufacturer to manufacturer. PUF tends to be a non-homogeneous product containing a number of additives and artifacts in variable quantities from lot to lot. Due to this variation, sorbent quality control is even more critical than for XAD resins. It is important to get PUF products from the same manufacturer and, depending upon the application, from the same production lot. It is possible to reduce native sorbent contamination significantly prior to use as a collection media. Although the contaminants can not be removed entirely, they can be lowered sufficiently so as to allow determination of target compounds at acceptable detection limits. Solvent extraction is the preferred method for sorbent clean-up prior to use as sample collection media.

XAD-2 vs PUF

Either XAD-2 or PUF are suitable sorbents for the collection of semi-volatile organic compounds. The previous discussion highlighted some of the advantages and disadvantages of each; however, there are some other considerations. The most important is to determine the specific compounds of interest. The resin XAD-2 is better for collecting low molecular weight organics, and if these compounds are specifically targeted then PUF is unsuitable as a vapour trap. It is also possible to use a sandwich arrangement of PUF/XAD/PUF which allows for analysis of several different compound classes. The drawbacks are that there is increased resistance to air flow and that even more care must be taken when preparing equipment for sampling and, after sample collection, for analysis.

5.5.2.3 Volatile Organic Compounds

There are two principle methods of sampling ambient air for volatile organic compounds; by solid sorbent and by evacuated canister. Both methods use programmable timers to turn the sampling equipment on and off at prescribed times. It is also helpful if the sampling train includes an elapsed time counter and/or a chart recorder to check sampling duration and flow rate.

Solid Sorbents

Many different solid sorbents are available for ambient air sampling, including, but not restricted to, Tenax® GC, Florosil®, Spherocarb®, Carbotrap®, and Carbosieve®. Often, two or more sorbents are used in series. For example, Carbotrap®, which collects organic compounds from about C4 to C5 up to large molecules and Carbosieve®, which collects smaller airborne molecules such as the C2 hydrocarbons. Tenax® GC has been used extensively in the past but it does not capture highly volatile organics well (e.g. vinyl chloride) and samples with a high moisture content cause more problems than for sorbents such as Carbotrap® and Carbosieve®.

Generally, compounds trapped by this method are non-polar and non-reactive organics having boiling points in the -15 to +120 °C range. Ambient air is drawn through a cartridge containing about 0.04 g of Carbosieve® "S" (60/80 mesh; bed height about 30 mm) and 0.2 g of Carbotrap® "B" (20/40 mesh; bed height about 20 mm). Air flow is controlled by a mass flow controller. The sampling flow rate will depend upon the duration over which the sample is to be collected, the type and amount of sorbent(s) used, and the sensitivity of the analytical method. For example, for the two-sorbent combination mentioned above, 25 mL/min for 24 hours is satisfactory if the analytical method is GC-FID (gas chromatography with a flame ionization detector). Higher flow rates over shorter time periods are possible; however, it is important to determine the breakthrough volume of the sampling system before deciding on flow rate and sampling duration.

For the two-sorbent combination mentioned above, it is important to ensure that the Carbotrap® sorbent is upstream (i.e. exposed to the air flow first) when installing the cartridge to collect a sample. When analyzing the sample, the air flow is reversed. If the air flow is not reversed, during the desorption stage the larger molecules on the Carbotrap® sorbent get trapped on the Carbosieve® sorbent which has a very high affinity for these compounds and so these large molecules then do not come off the cartridge into the analytical system.

Evacuated Canisters

Although only a recent development in ambient air sampling, evacuated canisters are already in widespread use. This method is also referred to as whole-air collection because the air sample is collected in a canister rather than passed over a sorbent which collects the compounds of interest. Canisters are commercially available in sizes of 0.8, 3, 6, and 16 litres internal volume and, using a patented process, are specially treated to minimize both wall losses and sample/wall reactions.

Canisters are filled either by vacuum or by pumping depending upon whether greater than atmospheric fill pressures are required. Vacuum-filled sample collection involves filling the canister from vacuum to ambient or near-ambient pressure by using the initial canister vacuum to provide the differential pressure necessary to establish the collection flow (McClenny et al., 1987). The flow rate may be adjusted to suit the application by using various restriction devices. For instance, grab samples may be collected in as little as 10 to 30 seconds using no restriction, or time-integrated samples may be collected using needle valves or mass flow controllers to achieve a reasonably constant flow rate over the desired sampling duration.

Pumped sampling is generally used when long-term integrated samples or large sample volumes are required. A typical application is the collection of 24 hour samples on a periodic basis; e.g. every sixth day. The canister is filled using a pump and flow restructure arrangement to obtain a 15 to 30 psi fill pressure. Generally, a mass flow controller is used to ensure a constant fill rate and to compensate for the changing canister pressure during the sampling period (McClenny et al., 1987).

Cartridge vs Canister

There are advantages and disadvantages of both methods described above. Both methods yield detection limits in the sub-microgram per cubic metre range. The cartridge system has very little potential for contamination as the sample air is passed over the sorbent before any of the sampling train is encountered. The system is relatively inexpensive and analysis of multiple cartridges is readily automated. The major drawbacks are fragile glass cartridges which, when broken, cause the sample to be lost, and the analysis by thermal desorption is a one-shot affair. There is no way to re-analyze a sample if the results are suspect.

Using canister-based samplers there is potential for sample loss or contamination in the sampling train because the collector is at the downstream end of the system. Automated analysis of multiple canisters is unwieldy and the sampling equipment tends to be expensive. On the positive side, multiple analyses of a single sample are possible. This has very useful application for routine QA/QC work and re-analysis of individual samples if the original analysis results are suspect.

5.5.3 Real-Time Air Monitoring

5.5.3.1 Real-Time Total Hydrocarbon Analyzers (THC)

A total hydrocarbon analyzer (THC) may be used for continuous monitoring and recording of total hydrocarbons near or around a clean-up. Samplers should be located near the property line downwind from the site according to the prevailing wind direction. Equipment must be installed in a temperature controlled shelter large enough to support additional equipment such as fuel (hydrogen), calibration gases, and a continuous supply of clean air.

The measuring principle used in a THC analyzer is Flame Ionization Detection (FID) or Photoionization Detection (PID). The detectors should have a sensitivity of approximately 0.1

ppm methane over a 0 - 100 ppm range. Auto-ranging capabilities allow the analyzer to switch to a higher range automatically.

Since this unit is a non-specific analyzer, only the total of all volatile organic compounds present is measured. Individual compounds in a mixture cannot be analyzed by this method and may require additional equipment such as solid sorbents and evacuated canisters (See section 5.5.2.2). This additional equipment can be triggered automatically when elevated THC are detected by the continuous analyzer. Samples can then be collected and analyzed by the laboratory for the individual compounds.

For real-time determination of specific compounds, portable field GC analyzers are available. These portable GC's use a photoionization detector (PID) with sensitivity in the ppb range. Analysis is performed immediately, avoiding further laboratory support. A computer data link can provide real-time continuous sampling from the portable GC to a remote area.

5.5.3.2 Real-Time Particulate Monitoring (inhalable particulates)

Real-time particulate monitoring (PM-10) can be used for continuous sampling and recording of inhalable particulates. Monitoring of inhalable particulates can be done on a daily basis using a modified Hi-Vol sampler with a 10 micron cut-off head.

There are several types of monitors, each having a different measuring principle, but accomplishing the same result. The TEOM monitor is a true gravimetric instrument. It draws ambient air through a filter at a constant flow, continuously weighing the filter and calculating near instantaneous (10 min) mass concentration. In addition, the instrument computes the total mass accumulation on the collection filter, as well as 30 minute, 1 hour, 8 hour, and 24 hour averages of mass particulate concentration in air.

Another suitable unit is the Beta Guage real-time particulate monitor. Air is drawn in at a constant flow rate via a sampler unit. Samples of particulate matter are collected or precipitated on a filter tape. The measurement is carried out using the radiometric principle of beta absorption. Beta radiation is passed through the dust collection station of the filter strip by a beta ray emitting source (K^{85} or C^{14}) integrated into the instrument.

5.5.3.3 Real-Time Meteorological Information

The continuous measurement of wind speed (WS), wind direction (WD), temperature and barometric pressure is valuable for data validation and complaint investigation as to time and day of particular occurrences. Also, if a network of portable equipment is installed around the site, wind direction information may assist in determining which samplers should be operating or what samples should be analyzed to provide the most useful information. Temperature and barometric pressure information are needed for air sample volume calculations.

5.5.3.4 Data Acquisition Systems

To obtain real-time information and automatic storage of analyzer data from field stations, a telemetry and data acquisition system can be installed. Specialized reports and alarm parameters can automatically alert staff of elevated readings.

5.5.4 General QA and QC for Air Sampling

General QC for particulate sampling has been discussed under Section 5.5.2.1, Particulate.

All samples should be transported to the field in coolers with freeze packs. VOC samples should be collected within three days or less after the sample has been exposed. All samples should be shipped or taken to the analytical laboratory in coolers with freeze packs. VOC samples should be refrigerated and analyzed within three weeks. SVOC samples should be extracted at which point they may be frozen for analysis at a later date.

VOC samples collected in evacuated canisters need not be shipped in coolers with freeze packs.

It is important that smoking not be permitted near any of the sampling equipment; VOC tubes; SVOC filters or sorbents. It is also important that personal care products (perfume, cologne, aftershave) not be used near open VOC tubes.

It is recommended that at the analytical laboratory and at the field site office, a refrigerator be dedicated to air samples. Between sampling periods, shipping containers should not be stored near garages or areas where solvents are used.

Duplicate sampling, field blanks, and travel blanks are recommended to ensure the integrity of the sampling program.

5.5.5 Concluding Remarks

More detailed information is available from documents in the list of references and further reading at the end of this document. Analytical methods are described in section 8.5.

6. PROJECT QUALITY ASSURANCE AND QUALITY CONTROL

6.1 Introduction

The "quality" of data is a function of the uncertainty of the data compared to its end-use requirements. Thus, data can be acceptable under one requirement and be unacceptable under another. Quality management (QM) is the mechanism by which data are produced to meet a defined standard of quality with a stated degree of confidence. Quality assurance (QA) quantifies the accuracy and uncertainty associated with reported data. Quality control (QC) is the series of activities in the field or in the laboratory used to obtain and maintain that standard.(see definitions in Section 1.2)

Quality assurance and quality control are important elements in all facets of a project. They are mechanisms whereby the proponent can monitor the performance and results of staff or contractors, and they permit the regulatory agency to determine the quality of data submitted as part of a project review. The complexity of environmental data and the need for comparability has led to requirements for quality assurance and control in the analytical laboratory without necessarily recognizing that quality assurance and control must be applied throughout the program. For example, poor sampling or sample handling practices can obviate the most careful laboratory analyses.

Quality Management should not be considered as just another requirement by the proponent; it should be recognized that it is in the proponent's best interests to provide quality data, since it is that data which will be used to determine the need for remediation as well as remediation strategies.

In planning for a sampling and analysis program, management must determine the overall quality of data that will be considered to be acceptable and specify what steps will be taken when data does not meet the required quality. Thus, a critical planning step is the determination of Data Quality Objectives (DQOs). DQOs are statements that provide the definition of confidence required in drawing conclusions from the resulting data. For sampling for site clean-ups, the DQOs may often be dependent on the level of contamination present: that is, since the purpose of the sampling may be to differentiate materials with contaminant concentrations above a guideline from those below the guideline, a manager may require a higher quality of data for the testing of materials which may have concentrations near a guideline than for materials that are either more highly contaminated or for relatively clean materials. The process of setting DQOs and determining what actions will be taken if DQOs are not met necessitates an examination of sources of both error and variability, as well as the detailing of what procedures will be conducted to both reduce error to within acceptable limits and to understand and properly account for variability.

There are five important elements to consider in Quality Management of site clean-up projects.

- completeness of the data set;
- representativeness of the data;
- comparability of data;

- validity of identification; and
- accuracy and reproducibility of quantification.

Completeness of the measurement can be defined as obtaining the amount of data that is necessary to meet the project objectives.

The representativeness of the data is the degree to which data accurately and precisely represent the concentrations of the constituents or the characteristics of the material. For example, a sampler samples the top 10 cm of soil. If 1 m of material is removed, then the sample represents only the top 10% of the material.

The comparability of data is defined as the degree of confidence with which one data set can be compared to another or to guideline concentrations. This requires that proponents use consistent and documented methods throughout the data collection. Recognizing that sampling and analytical methods are constantly being changed and improved, the Ministry may accept non-standard procedures after consultation with the proponent.

The validity of identification is important for environmental samples where the analyst is asked to determine low concentrations of contaminants in complex matrices. This is particularly true for trace organic compounds (e.g., PCB).

The accuracy and reproducibility of quantification are the elements which most people use to define quality. Quantitative measurements are only estimates with a stated degree of uncertainty. Measurements should be made in a sufficient number and way so as to provide a statistically acceptable definition of the degree of confidence. This will require the analysis of a number of replicate samples by the analytical laboratory and the analysis of standard reference materials. The results of these additional analyses should be included with reports.

6.2 Elements of Site Clean-up Quality Management Program

The basic elements of a QM program include:

- technical competence of staff;
- suitability of facilities and equipment;
- good measurement practices;
- standard operating procedures;
- special operating procedures; and
- good documentation.

Good measurement practices can be defined as those procedures which have been tested and refined so that the results are consistently accurate and precise. Such practices can range from ensuring that equipment is routinely maintained and calibrated to procedures for the cleaning of sample containers. Typically such procedures are not documented but are assumed; unfortunately because they are not documented, such practices are variable even within a department.

Standard operating procedures are those procedures which specify how samples are to be collected, handled and analyzed. Such procedures should include the necessary information so that the techniques used can be repeated by another group or laboratory. Similar to the good measurement practices, standard operating procedures are typically not documented except where a laboratory is required to use a method published in a laboratory manual. Such operating procedures must include the procedures necessary to calibrate the techniques or to position the sampling equipment.

Most laboratory procedures are documented and would therefore be classified as standard operating procedures. However, sampling and sample handling procedures are often not documented and therefore special operating procedures should be developed and documented. These procedures should be developed with the assistance of well-qualified staff to ensure that all relevant points are included.

In each stage of the program, documentation of the procedures and techniques is important. It is in the proponent's best interests to ensure that all procedures are carefully and thoroughly documented, including obtaining relevant documentation from the laboratory. Full documentation will also ensure that the same techniques are used each time samples are collected and analyzed, thus permitting comparison of the data.

Summary
Sampling Planning Guide

1. Identify Objectives
   These could include any or all of:
   · establish baseline data
   · monitor impacts of discharge
   · research on fate and effects
   · establish suitability of materials

2. Planning
   Desk-Top Activities
   · assemble all historical and current information
   · using suitable maps identify:
     - water uses
     - access points
     - extent of study area
     - sources (discharge points)
     - plot information from historical/ preliminary studies
   · determine sampling density in consideration of:
     - statistical requirements
     - sources of contaminants
     - extent of contamination
     - historical information
   · determine study components using:
     - known sources or extent of contamination
     - chemical behaviour of contaminants, including expected pathways of exposure or uptake by organisms
     - regulatory requirements (e.g., PSQGs, PWQOs, clean-up criteria)
   Field Activities
   · reconnaissance survey
     - verify historical information
     - verify sources/discharges
     - determine equipment necessary
   · select appropriate sampling devices
   · sampling schedule including contingency plans

3. Sample Collection
   · collect into appropriate containers
   · collect required quantities
   · ensure appropriate handling, preservation and storage
   · ensure required protocols are followed based on requirements of analytical labs.
   · ensure appropriate number and type of field QC samples

4. Laboratory Analysis
   - ensure appropriate MDL criteria/capabilities
   - ensure performance monitoring, control and reporting
   - request appropriate documentation for methods and QC samples
   - determine if data is corrected by lab for any performance factors
   - determine if lab is accredited for any/all potential contaminants and matrices

5. Data Interpretation
   - apply tests and analyses appropriate to the study objectives
   - determine need for statistical analysis
   - determine potential need for additional/confirmatory sampling and analysis
   - determine potential impacts of field and laboratory QC on findings

7. FIELD QUALITY ASSURANCE AND QUALITY CONTROL

7.1 Introduction

The sampling plan that is developed prior to sampling should include the detailing of procedures to assure that the quality of the samples and information collected is acceptable. Project Quality Management (QM) principles are presented in Section 6. Laboratory quality control and assurance practices are discussed in Section 8. The current section deals with field QA and QC.

During the planning stages for sampling, potential sources of error and of variability should be listed and quality control checks (QC) should be specified for each. The method of documentation of the results of these QC checks should be stated.

Field QC plans should detail the types of field observations that are to be made during the sampling and the terminology to be used in describing them. Details such as soil horizon depth, sediment colour, boundary type, texture, odours, water colour, meteorological conditions (air sampling), etc. can be important later in interpreting the results of the sampling, as well as during the remediation phase.

The sampling plan should specify the number and type of field QC samples that field personnel should submit to the lab. Field replicates should be submitted systematically. In addition, reference samples (i.e. a sample that is submitted with each batch of samples for comparing batch to batch variability) should be submitted at predetermined frequencies.

Throughout all sampling and sample handling, care must be taken to prevent cross contamination of samples. Sampling equipment should be cleaned carefully between sites, and appropriate, clean sample containers used. It is advisable for sampling to proceed from the least contaminated sites to the most contaminated sites in order to minimize the potential for cross contamination.

7.2 Types and Frequency of Field QC Samples

A travelling blank is a sample of uncontaminated water free of the analytes of interest that is prepared by the laboratory performing the analysis, brought to the sampling site, opened at least as long as the manual sampling interval or while sampler bottles are being changed and preserved as necessary, closed and then returned to the lab for analysis. This sample will help to identify the presence of field and/or laboratory contamination which must be minimized and preferably eliminated.

The criteria or control limits for blank corrections must be determined by the laboratories on the basis of historical data and these must be documented.

A travelling spiked blank is a sample of uncontaminated matrix (water, soil, sediment, air absorbent) free of any interfering substances to which a known amount of standard solution and appropriate preservative have been added by the laboratory performing the analysis. The travelling spiked blank must be prepared within 24 hours of accompanying the containers required for sampling at the site, unless test specific protocols dictate a shorter time period.

The travelling spiked blank is brought to the field and returned, unopened, to the same laboratory for analysis. This sample will help to identify the stability and recovery of the contaminants of interest during the field/laboratory/transportation activity. All efforts should be directed to maximize the % recovery of the contaminants in these samples.

The travelling spiked blank must be spiked with solutions containing all the target parameters required to be analyzed at a level of 5-10 X the concentrations of interest at the specific site.

A replicate sample is any additional sample collected at the same time as another in a manner that minimizes differences. When an autosampler is used for water, samples contained in separate containers may be considered to be replicates; otherwise, samples must be collected using two automatic samplers installed at the same sampling location. Also referred to as field duplicates, these samples will help to establish estimates of variability of the matrix and site contaminant levels.

Replicate samples should be collected for all test groups, and travelling blank samples should be prepared and analyzed for all test groups except pH and conductivity at the frequencies listed above.

Travelling spiked blanks should be prepared and analyzed for all organics analyses, except Dioxins, Furans and solvent extractables.

Table 7.1A provides a summary of the field QC samples considered appropriate for each matrix referred to in the guideline. These should be considered as minimum recommendations to be increased as necessary based on the results obtained.

Table 7.1A Summary of Recommendations for Types and Frequency of Field QC Samples

MATRIX	FIELD QC SAMPLE TYPE		
	TRAVELLING BLANK	TRAVELLING SPIKED BLANK	REPLICATE (Field Duplicate)
Soil			✓
Sediment			✓
Water	✓	✓	✓
Air	✓**		✓
	At least one per remediation site. Approximately 1% of samples taken	At least one per remediation site. Approximately 1% of samples taken.	At least one per remediation site. Number required is highly variable.***
	FREQUENCY OF USE *		

* Note the frequency of use of the field QC types is independent for each matrix of interest being sampled and analyzed. Therefore, if soil, sediment, and water were being sampled, this guideline is recommending a minimum total of 5 field QC's be taken. One replicate for each of soil and sediment (total of 2), plus 1 of each field QC type for water (total of 3).

** Recommended for VOCs for cartridge technique. Use for other compounds where shipping and handling techniques have potential for additional contamination.

*** The number required is dependant upon both the knowledge of variability required and the precision needed for the resultant numbers. More replicates give better indications of estimated values. Where parameters are known to be variable, more replicates are required.

Note that these are recommended minimums, and that additional QC samples should be taken for any media where professional judgement indicates that they may be necessary to obtain the desired accuracy or precision.

8. ANALYTICAL METHODS AND LABORATORY QUALITY ASSURANCE AND QUALITY CONTROL

Introduction

Since the results of chemical analysis are to be compared to guideline criteria, it is essential that well documented, controlled and consistently applied analytical methods be utilized and that reasonable quality assurance and quality control procedures be carried out. Analytical methods and QC protocols must be referenced to recognized standard setting organizations (e.g. MOEE, APHA, USEPA, ASTM). Alternate equivalent methods must meet MDLs (Method Detection Limits) as detailed in this section, and must exhibit acceptable and comparable precision and accuracy.

Materials presented in this document should be utilized by proponents and reviewers to check that the data resulting from laboratory analysis are of sufficient quality upon which to base remediation decisions. For example, results should be checked to be sure that MDLs are being met, or that exceedences of MDLs that may occasionally occur are inconsequential and well explained.

Laboratory participation in a recognized accreditation program, such as the one provided by CAEAL (Canadian Association for Environmental Analytical Laboratories), is recommended as an indication of sound quality management practice.

8.1 Laboratory Quality Assurance and Quality Control

The quality of data depends upon planning, sampling, analysis and reporting. There are errors associated with each step. The role of quality management is to identify, measure and control these errors. Laboratories must be able to provide evidence that the quality of their data will meet the specific DQO's of a clients project. Therefore, it is necessary that all laboratories participating in environmental analysis must have a sound quality management program. Attainment and documentation of quality is ultimately linked to the development and implementation of documented control processes. These require quality planning, management, assurance, control, and monitoring. Such a program can be accomplished through the adoption of a program such as the quality Management Protocol given in the Ontario Ministry of Environment and Energy Publication "Protocol for the Sampling and Analysis of Industrial/Municipal Wastewater," (MOEE, 1994a). This document describes protocols for sampling and analysis of wastewater; however, the concepts/principles can be applied to any media that are to be analyzed in site clean-ups.

All laboratories participating in the analysis of materials covered by MOEE policies must have a formal written description of a method used for analysis. Bench procedures must be documented in sufficient detail to ensure proper, uniform application and must be readily available to technical staff. When modifications are required because of sample matrix or other factors, they must be noted and appended to the appropriate analytical records.

The method must include the following as a minimum:

A detailed sample pretreatment/preparation, clean-up (if required), instrumental measurement method, and data reporting procedure.

Pre-service QC:

- labware and reagent blanks;
- instrument setup standard;
- reference standard to validate in-house standards;
- certified reference material to validate method recovery;
- instrument detection limits (IDLs) and detector linearity curves (minimum of 5 point calibration);

In-service QC:

- baseline drift blanks;
- standards;
- instrument checks;

Run quality QC:

- method recovery blanks;
- method blanks;
- in-house matrix check material;
- duplicates (minimum of one set per run of 30 samples). For the purpose of this guidance, a duplicate sample is defined as a second aliquot from the same sample container.
- surrogates (added prior to organic extraction). The surrogates should be selected to cover the whole range of the particular scan. It is recommended to use a minimum of three surrogates per organic type scan, except PCBs, where one surrogate can be used.
- spiked samples, if applicable.

Method detection limits (MDLs) of each parameter.
The MDL should be determined according to the Ontario Ministry of the Environment protocol given in "Estimation of Analytical Method Detection Limits", (see Appendix A). Note that for inorganic soil/sediment determinations, option a: low level, in-run duplicate data must be used.

A table of recovery data, giving average recovery, range, and relative standard deviation for each parameter should be given.

Data related to method performance, such as control limits for calibration standards, standardization, duplicates, surrogates recoveries, and recovery of all the parameters in a group/scan should be appended to the method.

8.1.1 Guidelines for Accepting Analytical Results

The acceptability of the laboratory data should include the following considerations:

i) The method performance criteria as outlined in Section 8.3 - 8.5 have been met.

ii) The results of all laboratory QC samples that are applicable to the matrix and contaminant groups of interest (method blank, duplicate, spiked blank, spiked sample) are within the statistically determined control limits. The analyst is expected to respond to any QC results which exceed the control limits.

iii) Recoveries of all surrogates (organic analyses) where applicable are monitored and reported.

iv) Each laboratory participating in analysis should provide a table of the precision and accuracy estimates associated with the reported results. This can be accomplished through periodic analysis of standard or certified reference materials as available for each contaminant group selected at appropriate concentrations.

v) The analytical data is to be reported without correction, unless correction is clearly identified and described.

8.2 Analytical Procedures and Methods Principles

The choice of analytical procedures and instruments is dependent on several requirements, including matrices to be analyzed, detection limits to be reached, comparability to guidelines, parameters analyzed, availability and suitability of techniques and instrumentation.

The procedures chosen take into consideration these requirements.

8.2.1 Inorganic Procedures

Sample Preparation / Processing:

In general there are four procedures: direct analysis, a mild extraction, a strong extraction, and a total analysis. Samples are analyzed directly if the instrumentation does not require adjustment to the sample, (e.g. drinking water by ICP - MS). This may provide total or partial results. A mild extraction is used if the program requires only the determination of "available" parameters, or if other techniques are not precise or are too involved. A strong extraction is used to separate the parameters from the matrix when strongly bound and to prepare the parameters for analysis by a particular technique, (e.g. metals in soil by ICP). Finally, a total extraction may include fusion, hydrofluoric acid, or XRF. These would be used when a determination of the total parameter is required, or if other extractions are very imprecise.

Sample Analysis:

In general, metals analysis can be carried out using colourimetry, X-Ray spectrometry, atomic absorption spectroscopy, or inductively coupled plasma atomic emission spectrometry. Colourimetric methods are frequently long and labour intensive. X-Ray offers multi-element analysis but does not have the low detection limits required for trace metal analysis. Where the levels are high enough in the sample and a total analysis is required, X-Ray can be used, (e.g. titanium in soil.) (Acid extraction of titanium is not very precise, and fusion techniques are not convenient.) Atomic Absorption has low detection levels but does only sequential analysis. ICP is the choice when low level, multi-elemental analysis is required.

The cold vapour and hydride vapour AAS techniques are used for mercury and hydride forming elements, (arsenic, selenium, antimony) because of their sensitivities.

The need for very low detection limit for uranium requires the use of ICP - Mass Spectrometry. Fluorometric techniques agree well with ICP - MS at higher levels. However, ICP - MS is fifty times more sensitive.

A wide range of colourimetric, ion selective, titration, and ion chromatographic techniques have been developed for use for chloride, fluoride, nitrogen, phosphorus, nitrate, nitrite, sulphide, and cyanide. These techniques are chosen based on sensitivity, ease of

sample preparation, requirements of programs and instrumentation.

Electrical conductivity and pH measurements are made on water extracted samples for convenience, allowing both measurements on the same solution.

Hexavalent chromium can be analyzed directly using colourimetric techniques as long as there are no interferences, (e.g. clear waters). Solid samples generally require an alkaline extraction followed by an APDC - MIBK extraction and AAS analysis. Spiking of the sample is required to ensure that there is no conversion of Cr (VI) or Cr (III).

Combustion techniques are used for sulphur since the results give a total concentration and requests for sulphur are usually for the single element. Where a metal scan is required and a digestion technique is available to do a total extraction of sulphur, ICP analysis is possible.

8.2.2 Organic Procedures

Dibenzo-p-dioxins/Dibenzofurans

This method is an isotopic dilution method where labelled analogs of PCDD and PCDF are added to the sample prior to extraction and results are corrected for the recovery of these compound isotopes. Mass spectrometric detection is needed to differentiate between the native PCDD, PCDF and the labelled PCDD, PCDF added.

Volatile Organic Compounds

Heated Purge & Trap/ Headspace: Purge and Trap without heat will not liberate the volatiles from solid matrices matrix. Headspace uses heat as well but caution should be taken to ensure that the requirements for detection limit are met.

GC/MS Analysis: Conventional detection for these parameters in water samples is often a combination of flame ionization with electron capture or photoionization with electrolytic conductivity. These detectors have limited specificity and when analyzing complex matrices, such as soil, could suffer from false positive results.

The use of mass spectral detection has become the standard for environmental analysis. The added level of confidence in compound identification, due to the monitoring of specific ions and ion ratios, as well as the decreasing costs associated with the purchase and maintenance of mass detection systems, justifies their use.

Polychlorinated Biphenyls

GC/MS or GC/ECD: There are two different environmentally enforceable quantitation techniques for PCB. The first was used at Smithville, Swan Hills and Goose Bay, to measure the destruction of PCB. This technique uses GC/MS, where congener groups are summed to give a total. The second technique is Araclor profile matching and quantitation using the sum of at least 12 of the more prominent peaks. For better sensitivity an electron capture detector is used. This method is used to measure PCB levels in water, soil, biota and oil.

Phenolics/Acid Compounds

GC/MS Analysis: The use of mass spectrometric identification/detection is recommended for this group of compounds. No other single detector can measure all of these compounds at the detection limits specified, with the same level of confidence. This extracted fraction tends to be very dirty and so there is a need to monitor specific ions and ion ratios to determine compound type.

Polycyclic Aromatic Hydrocarbons

This analysis is much the same as that for phenolics in that, the sample extract tends to be very dirty. Other methods for analysis include flame ionization detection of a gas

chromatographic extract and fluorescence detection from liquid chromatographic eluent. Flame ionization is not specific enough to differentiate between PAH and the numerous interferences found in this extract and liquid chromatography is not efficient enough to separate all of the PAH compounds.

Pesticides/Herbicides

The advantage of using GC/MS for this group is typical; better confidence in compound identification. All of these compounds can be analyzed in a single extract using GC/MS. Other methods, however, are very popular, such as electron capture detection of 3 separate extracts; one for the organochlorine pesticides, a second for the phenoxy acids and a third for the organophosphates. GC/ECD is an acceptable alternate technique when run on two different columns of different polarity.

8.3 Analytical Guidelines and Method Detection Limits (MDLs) for Soils and Sediments

Introduction to Tables

The following tables present the analytical method principles that should be used for comparison of contaminant concentrations with numeric criteria. Alternate equivalent methods must meet MDLs as detailed in this section and must exhibit acceptable and comparable precision and accuracy.

The method codes presented in the format;

E1234A

refer to methods in use by the MOEE and are included for reference purposes. They are only provided where there is a good match between the current MOEE method and the cited list of contaminants and MDL requirements. These detailed methods can be obtained for a minimal cost from the MOEE Laboratory Services Branch. The Method Guidelines and the MOEE reference method listed are intended to assist in the identification and quantification of the broadest range of contaminants listed in the tables. It is recognized that neither every MOEE method reference nor Method Guideline may be capable of analyzing every contaminant to the required MDL in all matrices of soil, sediment, water or air.

All MDLs presented in the tables are estimates that are realistically attainable for low level environmental concentrations, based on documented method performance, and/or consultation with other labs, using the listed methods and good laboratory practices. As such, the MDLs listed in the following tables represent the most stringent method performance criteria for this guideline. Where higher levels are expected or known to exist at a particular site, or where less stringent criteria are identified by the guideline, MDLs should be demonstrated by the contributing laboratory as about 1/10 of the numeric criteria that are appropriate for the site, as per the guideline document (MOEE, 1996).

The CAS# is the Chemical Abstract Service Registry number for the compound.

The MDLs presented are for both soils and sediments unless otherwise stated.

The reader is referred to Section 5.1.6 for pre-analysis sample preparation requirements.

All results for soils and sediments should be reported on a dry weight basis.

8.3.1 Dibenzo-p-dioxins/Dibenzofurans - Analytical Guidelines and Method Detection Limits (MDLs) for Soils and Sediments

Dibenzo-p-dioxins/Dibenzofurans	CAS#	MDL* Soils and Sediments (pg/g)	Method Guidelines
Octachlorodibenzo-p-dioxin	3268-87-9	6.3	**Sample Preparation:** An aliquot of soil is spiked with ^{13}C labelled analogs of the PCDD and PCDF prior to extraction. A minimum of one ^{13}C labelled 2,3,7,8 substituted isomer per congener group is required. The sample is extracted with toluene using a Soxhlet liquid-solid extraction. The extract is cleaned using a series of open liquid-solid chromatographic columns, and high performance liquid chromatography as necessary. **Instrumental Measurement:** GC/high resolution MS, tandem MS or low resolution MS. MOEE Method Reference: E3151B
Octachlorodibenzofuran	39001-02-0	11	
Total heptachlorinated dibenzo-p-dioxins	37871-00-4	3.8	
Total heptachlorinated dibenzofurans	38998-75-3	8.2	
Total hexachlorinated dibenzo-p-dioxins	34465-46-8	3.5	
Total hexachlorinated dibenzofurans	55684-94-1	3.8	
Total pentachlorinated dibenzo-p-dioxins	36088-22-9	4.4	
Total pentachlorinated dibenzofurans	30402-15-4	5.0	
Total tetrachlorinated dibenzo-p-dioxins	41903-57-5	1.6	
Total tetrachlorinated dibenzofurans	55722-27-5	1.6	
2,3,7,8-Substituted Isomers			
2,3,7,8-T_4CDD	1746-01-6	1.6	
1,2,3,7,8-P_5CDD	40321-76-4	4.4	
1,2,3,4,7,8-H_6CDD	39227-28-6	2.8	
1,2,3,6,7,8-H_6CDD	57653-85-7	3.5	
1,2,3,7,8,9-H_6CDD	19408-74-3	3.1	
1,2,3,4,6,7,8-H_7CDD	35822-46-9	3.8	
2,3,7,8-T_4CDF	51207-31-9	1.6	
1,2,3,7,8-P_5CDF	57117-41-6	5.0	
2,3,4,7,8-P_5CDF	57117-31-4	3.8	
1,2,3,4,7,8-H_6CDF	70648-26-9	2.5	
1,2,3,6,7,8-H_6CDF	57117-44-9	3.8	
2,3,4,6,7,8-H_6CDF	60851-34-5	3.1	
1,2,3,7,8,9-H_6CDF	72918-21-9	1.9	
1,2,3,4,6,7,8-H_7CDF	67562-39-4	5.7	
1,2,3,4,7,8,9-H_7CDF	55673-89-7	8.2	

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.3.2 Volatile Organic Compounds (VOCs) - Analytical Guidelines and Method Detection Limits (MDLs) for Soils and Sediments

Halogenated Compounds	CAS#	MDL* Soils and Sediments b(ng/g)	Method Guidelines
1,1,2,2-Tetrachloroethane	79-34-5	4.0	**Sample Preparation:** An aliquot of soil is weighed directly into a purge vessel. VOC-free water and minimum of three surrogates are added to the purge vessel. **Instrumental Measurement:** Heated purge and trap and GC/MS. Headspace - GC/MS technique may be applied.
1,1,2-Trichloroethane	79-00-5	2.0	
1,1-Dichloroethane	75-34-3	2.0	
1,1-Dichloroethylene	75-35-4	2.0	
1,2-Dichlorobenzene	95-50-1	2.0	
1,3-Dichlorobenzene	541-73-1	2.0	
1,4-Dichlorobenzene	106-46-7	2.0	
Bromoform (Tribromomethane)	75-25-2	2.0	
Bromomethane	74-83-9	3.0	
Carbon Tetrachloride	56-23-5	2.0	
Chloroform (Trichloromethane)	67-66-3	2.0	
Cis-1,3-Dichloropropylene	10061-01-5	2.0	
Dibromochloromethane	124-48-1	3.0	
Ethylene dibromide (1,2-dibromoethane)	106-93-4	4.0	
Dichloromethane (Methylene chloride)	75-09-2	3.0	
Tetrachloroethylene (Perchloroethylene)	127-18-4	2.0	
Trans-1,3-Dichloropropylene	10061-02-6	3.0	
Trichloroethylene	79-01-6	4.0	
Trichlorofluoromethane	75-69-4	3.0	
Ethylene dichloride (1,2-Dichloroethane)	107-06-2	2.0	
1,2-Dichloropropane	78-87-5	2.0	
Chlorobenzene	108-90-7	2.0	
Chloromethane	74-87-3	3.0	
Trans-1,2-Dichloroethylene	156-60-5	3.0	
Vinyl chloride (Chloroethylene)	75-01-4	3.0	
1,1,1-Trichloroethane	71-55-3	2.0	

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.3.2 Volatile Organic Compounds (VOCs) - Analytical Guidelines and Method Detection Limits (MDLs) for Soils and Sediments

Non-Halogenated Compounds	CAS#	MDL* Soils and Sediments (ug/g)	Method Guidelines
Benzene Styrene Toluene o-Xylene m-Xylene/p-Xylene Ethylbenzene	71-43-2 100-42-5 108-88-3 95-47-6 108-38-3 & 10642-3 100-41-4	2.0 2.0 2.0 2.0 2.0 2.0	**Sample Preparation:** An aliquot of soil is weighed directly into a purge vessel. VOC-free water and minimum of three surrogates are added to the purge vessel. **Instrumental Measurement:** Heated purge and trap and GC/MS or GC/PID. Headspace - GC/MS or GC/PID technique may be applied.
Petroleum Hydrocarbons ** (commonly referred to as TPH)			The basic principles are as follows;
Light (purgeables and extractables) (gasoline and/or diesel fuels)		10 µg/g	The sum of the total purgeables + C_{10} to C_{24} extractables. Purgeables are determined as above for BTEX, but quantified by integration of total area for the C5 - C10 compounds. Extractables are determined by soxhlet, microwave or ultrasonic extraction with hexane/acetone (1:1) followed by fractionation using silica gel, analysis by GC/MS or GC/FID and quantification by integrating total area in which the C10 - C24 compounds are eluted.
Heavy oils (extractables)		100 µg/g	A hexane/acetone (1:1) extract (soxhlet, microwave or ultrasonic) is fractionated using silica gel, dried, and analyzed gravimetrically.

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).
** Methods are under review

8.3.3 Polychlorinated Biphenyls - Analytical Guidelines and Method Detection Limits (MDLs) for Soils and Sediments

Polychlorinated Biphenyls (PCBs)	CAS#	MDL*	Method Guidelines
		Soils and Sediments (ng/g)	
Total PCBs (Aroclor 1242-1260)		300	**Sample Preparation:** An aliquot of soil is spiked with a minimum of 1 surrogate prior to extraction. The sample is extracted with organic solvent and the extract is cleaned as necessary. **Instrumental Measurement:** GC/MS, GC/ECD Quantitation is performed by Aroclor profile matching where at least 12 peaks are selected and compared to the corresponding Aroclor standard or mixture of standards. . MOEE Method Reference: E3270A

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.3.4 Phenolic/Acidic Compounds - Analytical Guidelines and Method Detection Limits (MDLs) for Soils and Sediments

Phenols/Acids	CAS#	MDL* Soils and Sediments (ng/g)	Method Guidelines
2,3,4,5-Tetrachlorophenol	4901-51-3	100.0	**Sample Preparation:** An aliquot of soil is spiked with a minimum of three isotopically labelled compounds. It is acidified and extracted with organic solvent. The extract is derivatized and cleaned as necessary. **Instrumental Measurement:** GC/MS
2,3,4,6-Tetrachlorophenol	58-90-2	100.0	
2,3,5,6-Tetrachlorophenol	935-95-5	100.0	
2,3,4-Trichlorophenol	15950-66-0	100.0	
2,3,5-Trichlorophenol	933-78-8	100.0	
2,4,5-Trichlorophenol	95-95-4	100.0	
2,4,6-Trichlorophenol	88-06-2	100.0	
2,4-Dimethylphenol	105-67-9	200.0	
2,4-Dinitrophenol	51-28-5	200.0	
2,4-Dichlorophenol	120-83-2	100.0	
2,6-Dichlorophenol	87-65-0	100.0	
4,6-Dinitro-o-cresol	534-52-1	100.0	
2-Chlorophenol	95-57-8	100.0	
4-Chloro-3-methylphenol	59-50-7	100.0	
4-Nitrophenol	100-02-7	200.0	
m-Cresol	108-39-4	100.0	
o-Cresol	95-48-7	100.0	
p-Cresol	106-44-5	100.0	
Pentachlorophenol	87-86-5	100.0	
Phenol	108-95-2	100.0	

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.3.5 Polycyclic Aromatic Hydrocarbons (PAHs) - Analytical Guidelines and Method Detection Limits (MDLs) for Soils and Sediments

Polycyclic Aromatic Hydrocarbons (PAH) - Base Neutral Extractables	CAS#	MDL*	Method Guidelines
		Soils and Sediments (ng/g)	
Acenaphthene	83-32-9	50.0	**Sample Preparation:** An aliquot of soil is spiked with D8 naphthalene and a minimum of two other isotopically labelled compounds (surrogates) prior to extraction. The sample is extracted with organic solvent and the extract is cleaned as necessary. **Instrumental Measurement:** GC/MS MOEE Method Reference: E3350A
5-nitro Acenaphthene	602-87-9	100.0	
Acenaphthylene	208-96-8	50.0	
Anthracene	120-12-7	50.0	
Benz(a)anthracene	56-55-3	50.0	
Benzo(a)pyrene	50-32-8	50.0	
Benzo(b)fluoranthene	205-99-2	50.0	
Benzo(g,h,i)perylene	191-24-2	100.0	
Benzo(k)fluoranthene	207-08-9	50.0	
Camphene	79-92-5	50.0	
1-Chloronaphthalene	90-13-1	50.0	
2-Chloronaphthalene	91-58-7	50.0	
Chrysene	218-01-9	50.0	
Dibenz(a,h)anthracene	53-70-3	100.0	
Fluoranthene	206-44-0	50.0	
Fluorene	86-73-7	50.0	
Indeno(1,2,3-cd)pyrene	193-39-5	100.0	
Indole	120-72-9	50.0	
1-Methylnaphthalene	90-12-0	50.0	
2-Methylnaphthalene	91-57-6	50.0	
Naphthalene	91-20-3	50.0	
Perylene	198-55-0	50.0	
Phenanthrene	85-01-8	50.0	
Pyrene	129-00-0	50.0	

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.3.6 Pesticides/Herbicides - Analytical Guidelines and Method Detection Limits (MDLs) for Soils and Sediments

Pesticides/Herbicides	CAS#	MDL* Soils and Sediments (ng/g)	Method Guidelines
Aldrin	309-00-2	50	**Sample Preparation:** An aliquot of soil is spiked with a minimum of three isotopically labelled compounds (surrogates) prior to extraction. The sample is extracted with organic solvent and the extract is cleaned as necessary. **Instrument Measurement:** GC/MS or dual column GC/ECD. For non-MS techniques, surrogates are not required. MOEE Method Reference: E3270A
Chlordane		50	
O,P-DDT	789-02-6	50	
P,P-DDT	50-29-3	50	
DDE	72-55-9	50	
DDD	72-54-8	10	
Dieldrin	60-57-1	50	
Endrin	72-20-8	20	
Endosulfan I	959-98-8	40	
Endosulfan II	33213-65-9	40	
Endosulfan III	1031-07-8	50	
Heptachlor	76-44-8	50	
Heptachlor epoxide	1024-57-3	50	
Hexachlorobenzene	118-74-1	10	
Hexachlorobutadiene	87-68-3	10	
Hexachlorocyclohexane, gamma (Lindane)	58-89-9	10	
Hexachloroethane	67-72-1	10	
Methozychlor	72-43-5	50	
Toxaphene	8001-35-2	1000	
Trichlorobenzene		20	

Pesticides/Herbicides	CAS#	MDL* Soils and Sediments (ng/g)	Method Guidelines
Diazinon Methyl Parathion Parathion	333-41-5 298-00-0 56-38-2	50 50 50	**Sample Preparation**: The sample is extracted with organic solvent under neutral pH conditions and cleaned as necessary. **Instrument Measurement**: GC/MS , Dual Column GC/TSD, NPD MOEE Method Reference: E3224A
Carbaryl	63-25-2	30	**Sample Preparation**:Same as above **Instrument Measurement**:HPLC/UV MOEE Method Reference: E3158A
Silvex 2,4, D	93-72-1 94-75-7	100 100	**Sample Preparation:** sample is extracted under acidic conditions using an organic solvent. Extract is derivatized and cleaned as necessary. **Instrument Measurement:**GCMS or dual column GC/ECD. MOEE Method Reference: E3119A

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.3.7 Inorganics - Analytical Guidelines and Method Detection Limits (MDLs) for Soils and Sediments

PARAMETERS	CAS #	MDL* µg/g	METHOD GUIDELINES
Copper		5.0	A sample (0.50 g) is digested with conc. nitric and conc. hydrochloric acids in digestion tubes in a hot block digester, and analyzed by ICP. Where needed AAS or DCP can be used.
Nickel		2.5	
Zinc		25	
Cadmium		1.0	
Cobalt		2.5	MOEE Method References:
Chromium		5.0	Soil -E3073A, E3074A, E3075A
Lead		10	Sediment - E3062A,E3063A
Iron		1000	
Manganese		25	
Aluminium		1000	
Sodium		25	
Potassium		25	
Calcium		500	
Magnesium		250	
Vanadium		5.0	
Molybdenum		2.5	
Barium		2.5	
Beryllium		0.5	
Strontium		5.0	
Thallium		2.5	
Silver		0.25	A sample (0.500 g) is digested with nitric and sulphuric acids in digestion tube in a hot block digester, and analyzed by AAS. Where available ICP can be used. E3063A

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

PARAMETERS	CAS #	MDL* µg/g	METHOD GUIDELINES
Boron - hot water extract[1]		0.02	50 ml of 0.01 M $CaCl_2$ solution is added to 25 g of air-dried soil (<2 mm), then boiled for 5 min. Volume loss is made up and filtrate analyzed by ICP. AAS or DCP can be used.
Mercury		0.05	A sample (0.250 g) is digested with 4:1 sulphuric:nitric acid in a hot block digester, and analyzed by CV AAS. MOEE Method Reference: E3059A
Sulphur		50.0	A sample (0.250 g) is combusted with copper and iron accelerators in a combustion furnace. The evolved SO_2 is titrated with potassium iodate using starch as an indicator. MOEE Method Reference: E3096A
Fluoride		2.5	A sample (0.50 g) is extracted with 0.1N perchloric acid for 4 hours at 80°C. The sample is shaken for one hour. TISAB III M Buffer is added, and the solution is shaken for 15 minutes. The analysis is done by Ion Selective Electrode. MOEE Method Reference: E3063A
Nitrogen Phosphorus		0.5 (mg/g) 0.1 (mg/g)	A sample (0.08-0.40 g) is digested with conc. sulphuric acid followed by potassium persulphate. It is neutralized with sodium hydroxide, and analyzed by automated colourimetry. MOEE Method Reference: E3116A
Arsenic Selenium Antimony		1.0 1.0 1.0	A sample (0.06 g) is digested overnight with nitric:sulphuric:perchloric, (6:3:1) acid mixture. Hydrochloric acid is added, and the analysis is done by flameless AAS. MOEE Method Reference: E3245A

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

[1] Due to an observed potential for Boron contamination of purchased $CaCl_2$ and to the potential for boron contamination from glassware, it is very important for method blanks to be used and reported, and for corrective measures to be taken should blanks contain significant amounts of boron.

PARAMETERS	CAS #	MDL* µg/g	METHOD GUIDELINES
Titanium		8.0	A sample (0.25 g) is heated with lithium metaborate. The molten sample is mixed with 5% nitric acid and conc. hydrofluoric acid, and analyzed by ICP.
		100	A sample (4.0 g) is pressed into a pellet, and analyzed by XRF. MOEE Method Reference: E3327A
Uranium		1.0	A sample (0.20 g) is digested with conc. Nitric acid to dryness. The nitric acid is added again and evaporated.The analysis is done by ICP-MS. MOEE Method Reference: E3215A
		5.0	A sample (0.20 g) is digested with conc. nitric acid to dryness. The nitric acid is added and evaporated. The sample is co-precipitated with aluminium phosphate and extracted with ethyl acetate (see Standard Methods APHA, 1989, method 7500-UC). The analysis is done by Fluorometry.
Loss on Ignition		0.25%	A sample (1.00 g) is dried at 105° C for 16 hours then muffled at 475°C for 4 hours. Weight loss is then determined. MOEE Method Reference: E3139A

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

PARAMETERS	CAS #	MDL* µg/g	METHOD GUIDELINES
pH Electrical Conductivity		0.25 --	A sample (10 g) is shaken with 20 ml distilled water for 30 minutes, allowed to stand for 30 minutes, and analyzed by a pH meter and a conductance meter. MOEE Method Reference: E3137A - Conductivity E3137A- pH
Sodium Adsorption Ratio		--	Ratio is calculated from concentrations (me/l) of sodium, calcium and magnesium in extract from pH procedure as follows. SAR= $[Na]/(([Ca]+[Mg])/2)^{0.5}$
Nitrate + Nitrite		5.0	A sample (10 g) is extracted with distilled water by shaking for 30 minutes. Nitrate is reduced to nitrite with hydrazine in alkaline media containing cupric ion. Nitrite is diazotized with sulphanilamide, and the product coupled with ethylenediamine dihydrochloride. The analysis is done by colourimetry. MOEE Method Reference: E3208A
Cyanide (free)		0.05	A sample (5 g) is extracted with 50 ml distilled water by shaking for 30 minutes. The analysis is done by automated chloramine-T, barbituric acid-isonicotinic acid colourimetry. MOEE Method Reference: E3009A
Chloride (Water Extractable)		0.25	A sample (3 g) is extracted with distilled water (30ml)by shaking for 30 minutes. It is centrifuged, filtered (0.45 mm), and analyzed by ion chromatography. MOEE Method Reference: E3013A
Hexavalent Chromium		2.5	A sample (5 g) is digested using alkaline digestion. The solution is extracted with APDC-MIBK, and analyzed by AAS. Cr(iii) and Cr (vi) spikes are required.

All samples were initially sieved to ≤2.0 mm size.

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.4 Analytical Guidelines and Method Detection Limits (MDLs) for Surface Water and Groundwater Samples

Introduction to Tables

The following tables present the analytical method principles that must be used for comparison of contaminant concentrations with numeric criteria. Alternate equivalent methods must meet MDLs as detailed in this section and must exhibit acceptable and comparable precision and accuracy.

The method codes presented in the format;

E1234A

refer to methods in use by the MOEE and are included for reference purposes. They are only provided where there is a good match between the current MOEE method and the cited list of contaminants and MDL requirements. These detailed methods can be obtained for a minimal cost from the MOEE Laboratory Services Branch. The Method Guidelines and the MOEE reference method listed are intended to assist in the identification and quantification of the broadest range of contaminants listed in the tables. It is recognized that neither every MOEE method reference nor Method Guideline may be capable of analyzing every contaminant to the required MDL in all matrices of soil, sediment, water or air.

All MDLs presented in the tables are estimates that are realistically attainable for low level environmental concentrations, based on documented method performance, and/or consultation with other labs, using the listed methods and good laboratory practices. As such, the MDLs listed in the following tables represent the most stringent method performance criteria for this guideline. Where higher levels are expected or known to exist at a particular site, or where less stringent criteria are identified by the guideline, MDLs should be demonstrated by the contributing laboratory as about 1/10 of the numeric criteria that are appropriate for the site, as per the guideline document (MOEE, 1996).

The CAS# is the Chemical Abstract Service Registry number for the compound.

The MDLs presented are for both groundwater and surface water unless otherwise stated.

8.4.1 Dibenzo-p-dioxins/dibenzofurans - Analytical Guidelines and Method Detection Limits (MDLs) for Water

Dibenzo-p-dioxins/dibenzofurans	CAS#	MDL*	Method Guidelines
		Water pg/L	
Octachlorodibenzo-p-dioxin	3268-87-9	72	Samples are analyzed for tetra through octa chlorinated dibenzo-p-dioxins and dibenzofurans by isotope dilution mass. spectrometry. A known quantity of isotopically labelled PCDDs and PCDFs is added to each sample to serve as an internal quantitation standard. The sample is filtered through empole SPE disk. The disks are all eluted with ethanol/toluene.
Octachlorodibenzofuran	39001-02-0	35	
Total heptachlorinated dibenzo-pdioxins	37871-00-4	21	
Total heptachlorinated dibenzofurans	38998-75-3	28	
Total hexachlorinated dibenzo-p-dioxins	34465-46-8	28	
Total hexachlorinated dibenzofurans	55684-94-1	22	
Total pentachlorinated dibenzo-p-dioxins	36088-22-9	16	
Total pentachlorinated dibenzofurans	30402-15-4	21	
Total tetrachlorinated dibenzo-p-dioxins	41903-57-5	39	
Total tetrachlorinated dibenzofurans	55722-27-5	21	An alternative extraction procedure involving liquid/liquid extraction of the aqueous portion and Soxhlet extraction of particulates may be applied.
2,3,7,8-Substituted Isomers			
2,3,7,8-T_4CDD	1746-01-6	3.9	The extract is cleaned using a series of open liquid chromatographic columns. The final extract is analyzed by gas chromatography/high resolution mass spectrometry (GC/HRMS) or gas chromatography/tandem mass spec (GC/MSMS). Further clean-up using high performance liquid chromatography (HPLC) may be necessary prior to final analysis if the sample is highly contaminated with chemical interferences that are not removed by the open-column chromatographic clean-up.
1,2,3,7,8-P_5CDD	40321-76-4	16	
1,2,3,4,7,8-H_6CDD	39227-28-6	11	
1,2,3,6,7,8-H_6CDD	57653-85-7	15	
1,2,3,7,8,9-H_6CDD	19408-74-3	28	
1,2,3,4,6,7,8-H_7CDD	35822-46-9	21	
2,3,7,8-T_4CDF	51207-31-9	21	
1,2,3,7,8-P_5CDF	57117-41-6	21	
2,3,4,7,8-P_5CDF	57117-31-4	19	
1,2,3,4,7,8-H_6CDF	70648-26-9	14	
1,2,3,6,7,8-H_6CDF	57117-44-9	11	
2,3,4,6,7,8-H_6CDF	60851-34-5	22	
1,2,3,7,8,9-H_6CDF	72918-21-9	15	
1,2,3,4,6,7,8-H_7CDF	67562-39-4	28	MOEE Method Reference: E3164B
1,2,3,4,7,8,9-H_7CDF	55673-89-7	20	

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.4.2 Volatile Organic Compounds (VOCs) - Analytical Guidelines and Method Detection Limits (MDLs) for Water

Halogenated Compounds	CAS#	MDL*	Method Guidelines
		Water (µg/L)	
1,1,2,2-Tetrachloroethane	79-34-5	1.0	
1,1,2-Trichloroethane	79-00-5	1.0	**Sample Preparation**: An aliquot of sample
1,1-Dichloroethane	75-34-3	0.5	and a minimum of three surrogates are
1,1-Dichloroethylene	75-35-4	0.5	added to the purge vessel.
1,2-Dichlorobenzene	95-50-1	0.5	
1,3-Dichlorobenzene	541-73-1	0.5	**Instrument Measurement**:Purge and trap
1,4-Dichlorobenzene	106-46-7	0.5	GC/MS.
Bromodichloromethane	75-27-4	2.0	
Bromoform (Tribromomethane)	75-25-2	5.0	MOEE Reference: E3276A
Carbon Tetrachloride	56-23-5	2.0	
Chloroform (Trichloromethane)	67-66-3	1.0	Headspace - GC/MS or dual column
Dibromochloromethane	124-48-1	2.0	GC/FID, ECD may be applied
Ethylene dibromide (1,2 dibromoethane)	106-93-4	1.0	
Dichloromethane (Methylene chloride)	75-09-2	5.0	
Tetrachloroethylene (Perchloroethylene)	127-18-4	0.5	
Trichloroethylene	79-01-6	0.5	
Ethylene dichloride (1,2-Dichloroethane)	107-06-2	1.0	
1,2-Dichloropropane	78-87-5	0.5	
Chlorobenzene	108-90-7	0.5	
Trans-1,2-Dichloroethylene	156-60-5	0.5	
Vinyl chloride (Chloroethylene)	75-01-4	0.5	
1,1,1 Trichloroethane	71-55-3	0.5	
cis-1,2-dichloroethylene	156-59-2	0.5	
Bromomethane	74-83-9		
Cis-1,3-Dichloropropylene	10061-01-5		
Trans-1,3-Dichloropropylene	10061-02-6		
Trichlorofluoromethane	75-69-4		
Chloromethane	74-87-3		

MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.4.2 Volatile Organic Compounds (VOCs) - Analytical Guidelines and Method Detection Limits (MDLs)

Non-Halogenated Compounds	CAS#	MDL*	Method Guidelines
		Water (µg/L)	
Benzene	71-43-2	0.5	**Sample Preparation and Instrumentation:** same as above
Styrene	100-42-5	0.5	
Toluene	108-88-3	0.5	
o-Xylene	95-47-6	0.5	MOEE Reference: E3276A (excludes styrene)
m-Xylene/p-Xylene	108-38-3 & 10642-3	1.1	
Ethylbenzene	100-41-4	0.5	
Petroleum Hydrocarbons ** (commonly referred to as TPH)			The basic principles are as follows;
Light (purgeables and extractables) (gasoline or diesel fuels)		100	The sum of the total purgeables + C_{10} to C_{24} extractables. Purgeables are determined as above for BTEX, but quantified by integration of the total area for the C5 - C10 compounds. Extractables are determined by extraction with hexane followed by fractionation using silica gel, analysis by GC/MS or GC/FID and quantification by integrating total area in which the C10 - C24 compounds are eluted.
Heavy oils (extractables)		1000	The hexane extract is fractionated using silica gel, dried, and analyzed gravimetrically.

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).
** Methods are under review

8.4.3 Polychlorinated Biphenyls - Analytical Guidelines and Method Detection Limits (MDLs) for Water

Polychlorinated Biphenyls (PCBs)	CAS#	MDL*	Method Guidelines
		Water (µg/L)	
Total PCBs (Aroclor 1242-1260)	Unavailable	0.2	**Sample Preparation:** Water sample is extracted with an organic solvent under neutral pH conditions. Extract is cleaned on a Florisil column. **Instrumental Measurement:** GC/ECD Quantitation is performed by Aroclor profile matching where at least 25 peaks are selected and compared to the corresponding Aroclor standard or mixture of standards. MOEE Reference: E3120B

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.4.4 Phenolic/Acidic Compounds -Analytical Guidelines and Method Detection Limits (MDLs) for Water

Phenols/Acids	CAS#	MDL*	Method Guidelines
		Water (µg/L)	
2,3,4,5-Tetrachlorophenol	4901-51-3	0.2	**Sample Preparation:** A minimum of three surrogates are added to the sample The sample is then extracted with organic solvent, derivatized and cleaned as necessary. **Instrumental Measurement:** GC/MS MOEE Reference: E3265A
2,3,4,6-Tetrachlorophenol	28-90-2	0.4	
2,3,5,6-Tetrachlorophenol	935-95-5	0.10	
2,3,4-Trichlorophenol	15950-66-0	0.6	
2,3,5-Trichlorophenol	933-78-8	0.6	
2,4,5-Trichlorophenol	95-95-4	0.6	
2,4,6-Trichlorophenol	88-06-2	0.2	
2,4-Dimethylphenol	105-67-9	8.0	
2,4-Dinitrophenol	51-28-5	40	
2,4-Dichlorophenol	120-83-2	0.2	
2,6-Dichlorophenol	87-65-0	0.2	
4,6-Dinitro-o-cresol	534-52-1	25	
2-Chlorophenol	95-57-8	0.3	
4-Chloro-3-methyphenol	59-50-7	0.2	
4-Nitrophenol	100-02-7	1.5	
m-Cresol	108-39-4	0.5	
o-Cresol	95-48-7	0.5	
p-Cresol	106-44-5	0.5	
Pentachlorophenol	87-86-5	0.10	
Phenol	108-95-2	0.5	

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.4.5 Polycyclic Aromatic Hydrocarbons (PAHs) -Analytical Guidelines and Method Detection Limits (MDLs) for Water

Polycyclic Aromatic Hydrocarbons (PAH) - Base Neutral Extractables	CAS#	MDL*	Method Guidelines
		Water (µg/L)	
Acenaphthene	83-32-9	-	**Sample Preparation:** A minimum of three surrogates are added to ther sample which is then extracted with an organic solvent and cleaned as necessary. **Instrumental Measurement:** GC/MS
5-nitro Acenaphthene	602-87-9	-	
Acenaphthylene	208-96-8	-	
Anthracene	120-12-7	0.01	
Benz(a)anthracene	56-55-3	0.2	
Benzo(a)pyrene	50-32-8	0.05	
Benzo(b)fluoranthene	205-99-2	0.1	
Benzo(g,h,i)perylene	191-24-2	0.2	
Benzo(k)fluoranthene	207-08-9	0.01	
Camphene	79-92-5	-	
1-Chloronaphthalene	90-13-1	-	
2-Chloronaphthalene	91-58-7	-	
Chrysene	218-01-9	0.5	
Dibenz(a,h)anthracene	53-70-3	0.1	
Fluoranthene	206-44-0	0.2	
Fluorene	86-73-7	-	
Indeno(1,2,,3-cd)pyrene	193-39-5	0.2	
Indole	120-72-9	-	
1-Methylnaphthalene	90-12-0	-	
2-Methylnaphthalene	91-57-6	-	
Naphthalene	91-20-3	-	
Perylene	198-55-0	0.1	
Phenanthrene	85-01-8	0.1	
Pyrene	129-00-0	0.2	
2,4-Dinitrotoluene	121-14-2	0.2	

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.4.6 Pesticides/Herbicides - Analytical Guidelines and Method Detection Limits (MDLs) for Water

Pesticides/Herbicides	CAS#	MDL*	Method Guidelines
		Water (ug/L)	
Aldrin	309-00-2	0.01	**Sample Preparation:** Water Sample is extracted with organic solvent under neutral pH conditions. Extract is cleaned on a Florisil column, concentrated for instrument analysis. **Instrumental Measurement:** Dual column GC/ECD MOEE Reference: E3120B
Chlordane		0.02	
O,P-DDT	789-02-6	0.05	
P,P-DDT	50-29-3	0.05	
DDE	72-55-9	0.01	
DDD	72-54-8	0.05	
Dieldrin	60-57-1	0.02	
Endrin	72-20-8	0.05	
Endosulfan I	959-98-8	0.02	
Endosulfan II	33213-65-9	0.05	
Endosulfan III	1031-07-8	0.05	
Heptachlor	76-44-8	0.01	
Heptachlor epoxide	1024-57-3	0.01	
Hexachlorobenzene	118-74-1	0.01	
Hexachlorobutadiene	87-68-3	0.01	
Hexachlorocyclohexane, gamma (Lindane)	58-89-9	0.01	
Hexachloroethane	67-72-1	0.01	
Methoxychlor	72-43-5	0.05	
Toxaphene	8001-35-2	5.0	
Trichlorobenzene		0.05	

Pesticides/Herbicides	CAS#	MDL*	Method Guidelines
		Water (ug/L)	
Diazinon Methyl Parathion Parathion	333-41-5 298-00-0 56-38-2	0.2 0.5 0.2	**Sample Preparation:** Water Sample is extracted with organic solvent under neutral pH conditions,cleaned, and then concentrated for instrument analysis. **Instrumental Measurement:** Dual columnG C/TSD or dual column GC/NPD MOEE Reference: E3224A
Carbaryl (Sevin)	63-25-2	2.0	**Sample Preparation:** Same as above **Instrumental Measurement:** HPLC/UV MOEE Reference: E3158A
Silvex 2,4-D	93-72-1 94-75-7	0.2 1.0	**Sample Preparation:** Sample is extracted under acidic pH conditions using a C_{18} solid phase extraction cartridge. Extract is derivatized, cleaned and concentrated for instrumental analysis. **Instrumental Measurement:** GC/ECD MOEE Reference: E3119A

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.4.7 Inorganic Parameters - Analytical Guidelines and Method Detection Limits (MDLs) for Water Samples

Parameters	CAS#	MDL*	Method Guidelines
		Water (Particulates present) ug/L	
Copper		2.5 (10)	**Groundwater and Surface water - clean**
Nickel		1.0 (20)	No sample preparation; Analysis directly by ICP-MS, ICP-OES, or AAS
Zinc		1.0 (10)	
Cadmium		0.25 (10)	MOEE Method Reference:E3051A
Cobalt		0.1 (10)	
Chromium		2.5 (10)	**Groundwater and Surface water - particulates present**
Lead		0.2 (10)	Decant 50 ml and digest with hydrochloric/nitric acid to
Iron		30 (100)	12.5 ml (4 x concentration); analyze by ICP. The
Manganese		0.25 (10)	bracketed MDLs then apply.
Aluminium		0.50 (50)	MOEE Method Reference: E3094B.
Vanadium		0.25 (10)	
Molybdenum		0.25 (10)	
Barium		0.25 (10)	
Beryllium		0.25 (10)	
Strontium		0.5 (10)	
Boron		10	
Thallium		0.25 (10)	
Silver		0.25 (10)	
Titanium		2.5	
Uranium		0.25	
Sodium		500	Unpreserved sample analyzed by flame AAS
Potassium		250	MOEE Method Reference: E3217A
Calcium		1000	
Magnesium		250	

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

Parameters	CAS#	MDL*	Method Guidelines
		Water (µg/L)	
Mercury		0.1	Acidify sample with sulphuric and nitric acids and digest with potassium persulphate and potassium dichromate in a water bath. Analysis by CV AAS. MOEE Method Reference: E3060B
Sulphate		2.5 (µg/ml)	Sulphate separated by automated suppressed IC with conductivity detection. MOEE Method Reference: E3172A
Fluoride		0.05 (µg/ml)	Sample distilled in sulphuric acid at 160°C and reacted with Alizarin Fluorine Blue and Lanthanum nitrate. Analysis by colourimetry. MOEE Method Reference: E3221A
Nitrogen		.25 (µg/ml)	Kjeldahl digestion with analysis by colourimetry MOEE Method Reference: E3199A
Phosphorus		.10 (µg/ml)	Same as for nitrogen. MOEE Method Reference: E3200A
Arsenic Selenium Antimony		0.5 5.0 0.10	No sample preparation; Analysis directly by ICP-MS (Inductively coupled plasma mass spectrometry) MOEE Method Reference: E3051A

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

Parameters	CAS#	MDL*	Method Guidelines
		Water µg/ml.	
pH Electrical Conductivity		NA 5 µS/cm	Sample is shaken and poured into sample tube. Suspended matter is centrifuged and supernatant decanted. Analysis by pH meter and conductance meter. E3218A
Nitrate + Nitrite		0.25	Nitrate is reduced to nitrate in alkaline solution. Colourimetric determination based on formation of azo dye. E3193A
Cyanide (free)		0.005	Separation by in-line distillation. Analysis by automated chloramine-T, barbituric acid-isonicotinic acid colourimetry. E3014A
Cyanide (total)		0.005	Determined colourimetrically after manual distillation out of tartaric acid. E3015A
Chloride (Water Extractable)		1.0	Analyzed colourimetrically after reaction with mercuric thiocyanate. E3016A
Hexavalent Chromium		0.01	If no interferences are present, no preparation is needed. Analysis by colourimetry. E3056

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.5 Analytical Guidelines and Method Detection Limits (MDLs) for Air Samples

Introduction to Tables

The following tables present the analytical method principles that must be used for comparison of contaminant concentrations with numeric criteria. Alternate equivalent methods must meet MDLs as detailed in this section and must exhibit acceptable and comparable precision and accuracy.

The method codes presented in the format;

E1234A

refer to methods in use by the MOEE and are included for reference purposes. They are only provided where there is a good match between the current MOEE method and the cited list of contaminants and MDL requirements. These detailed methods can be obtained for a minimal cost from the MOEE Laboratory Services Branch. The Method Guidelines and the MOEE reference method listed are intended to assist in the identification and quantification of the broadest range of contaminants listed in the tables. It is recognized that neither every MOEE method reference nor Method Guideline may be capable of analyzing every contaminant to the required MDL in all matrices of soil, sediment, water or air.

All MDLs presented in the tables are estimates that are realistically attainable for low level environmental concentrations, based on documented method performance, and/or consultation with other labs, using the listed methods and good laboratory practices. As such, the MDLs listed in the following tables represent the most stringent method performance criteria for this guideline. Where higher levels are expected or known to exist at a particular site, or where less stringent criteria are identified by the guideline, MDLs should be demonstrated by the contributing laboratory as about 1/10 of the numeric criteria that are appropriate for the site, as per the guideline document (MOEE, 1996).

The CAS# is the Chemical Abstract Service Registry number for the compound.

8.5.1 Dibenzo-p-dioxins/dibenzofurans - Analytical Guidelines and Method Detection Limits (MDLs) for Air

Dibenzo-p-dioxins/dibenzofurans	CAS#	MDL*	Method Guidelines
		Air pg/m^3	
Octachlorodibenzo-p-dioxin	3268-87-9	0.058	Samples are analyzed for tetra through octa chlorinated dibenzo-p-dioxins and dibenzofurans by isotope dilution mass spectrometry. A known quantity of isotopically labelled PCDDs and PCDFs is added to each sample to serve as an internal quantitation standard. The samples are extracted with toluene using Soxhlet extractor. Extracts are cleaned using a series of open liquid chromatographic columns. The final extract is analyzed by gas chromatography/high resolution mass spectrometry (GC/HRMS) or gas chromatography/tandem mass spec (GC/MSMS). Further clean-up using high performance liquid chromatography (HPLC) may be necessary prior to final analysis if the sample is highly contaminated with chemical interferences that are not removed by the open-column chromatographic clean-up. MOEE Method Reference: E3122A
Octachlorodibenzofuran	39001-02-0	0.065	
Total heptachlorinated dibenzo-p-dioxins	37871-00-4	0.017	
Total heptachlorinated dibenzofurans	38998-75-3	0.036	
Total hexachlorinated dibenzo-p-dioxins	34465-46-8	0.025	
Total hexachlorinated dibenzofurans	55684-94-1	0.018	
Total pentachlorinated dibenzo-p-dioxins	36088-22-9	0.019	
Total pentachlorinated dibenzofurans	30402-15-4	0.017	
Total tetrachlorinated dibenzo-p-dioxins	41903-57-5	0.005	
Total tetrachlorinated dibenzofurans	55722-27-5	0.007	
2,3,7,8-Substituted Isomers			
2,3,7,8-T_4CDD	1746-01-6	0.005	
1,2,3,7,8-P_5CDD	40321-76-4	0.019	
1,2,3,4,7,8-H_6CDD	39227-28-6	0.025	
1,2,3,6,7,8-H_6CDD	57653-85-7	0.016	
1,2,3,7,8,9-H_6CDD	19408-74-3	0.022	
1,2,3,4,6,7,8-H_7CDD	35822-46-9	0.017	
2,3,7,8-T_4CDF	51207-31-9	0.007	
1,2,3,7,8-P_5CDF	57117-41-6	0.017	
2,3,4,7,8-P_5CDF	57117-31-4	0.016	
1,2,3,4,7,8-H_6CDF	70648-26-9	0.018	
1,2,3,6,7,8-H_6CDF	57117-44-9	0.014	
2,3,4,6,7,8-H_6CDF	60851-34-5	0.018	
1,2,3,7,8,9-H_6CDF	72918-21-9	0.018	
1,2,3,4,6,7,8-H_7CDF	67562-39-4	0.036	
1,2,3,4,7,8,9-H_7CDF	55673-89-7	0.032	

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.5.2 Volatile Organic Compounds (VOCs) - Analytical Guidelines and Method Detection Limits (MDLs) for Air

Halogenated Compounds	CAS#	MDL	Method Guidelines
		AIR (ng/m^3)	
1,1,2,2-Tetrachloroethane	79-34-5	500	**Sample Preparation:**
1,1,2-Trichloroethane	79-00-5	250	None Required.
1,1-Dichloroethane	75-34-3	100	Carbomolecular sieve cartridge sampling (7.2 L
1,1-Dichloroethylene	75-35-4	100	sampling volume)
1,2-Dichlorobenzene	95-50-1	1000	
1,3-Dichlorobenzene	541-73-1	500	**Instrumental Measurement:**
1,4-Dichlorobenzene	106-46-7	500	Thermal Desorption
1,3-Dichloropropene		500	GC/MS. At least 3 surrogates are spiked into
Bromoform (Tribromomethane)	75-25-2	-	the cartridge prior to desorption.
Bromomethane	74-83-9	-	
Bromodichloromethane		250	MOEE Method Reference: E3314A
Carbon Tetrachloride	56-23-5	100	
Chloroform (Trichloromethane)	67-66-3	100	
Cis-1,3-Dichloropropylene	10061-01-5	500	
Cis-1,2-Dichloroethylene		500	
Dibromochloromethane	124-48-1	-	
Ethylene dibromide (1,2-dibromoethane)	106-93-4	-	
Dichloromethane (Methylene chloride)	75-09-2	500	
Tetrachloroethylene (Perchloroethylene)	127-18-4	250	
Trans-1,3-Dichloropropylene	10061-02-6	-	
Trichloroethylene	79-01-6	250	
Trichlorofluoromethane	75-69-4	-	
Ethylene dichloride (1,2-Dichloroethane)	107-06-2	100	
1,2-Dichloropropane	78-87-5	200	
Chlorobenzene	108-90-7	250	
Chloromethane	74-87-3	-	
Trans-1,2-Dichloroethylene	156-60-5	100	
Vinyl chloride (Chloroethylene)	75-01-4	250	
1,1,1-Trichloroethane		100	

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.5.2 Volatile Organic Compounds (VOCs) - Analytical Guidelines and Method Detection Limits (MDLs) for Air

Non-Halogenated Compounds	CAS#	MDL*	Method Guidelines
		Air (ng/m^3)	
Benzene	71-43-2	200	same as for Halogenated VOCs
Styrene	100-42-5	1000	
Toluene	108-88-3	500	MOEE Method Reference: E3314A
o-Xylene	95-47-6	500	
m-Xylene/p-Xylene	108-38-3 & 10642-3	1000	
Ethylbenzene	100-41-4	500	

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.5.3 Polychlorinated Biphenyls - Analytical Guidelines and Method Detection Limits (MDLs) for Air

Polychlorinated Biphenyls (PCBs)	CAS#	MDL* AIR (ng/m^3)	Method Guidelines
Total PCBs (Aroclor 1242-1260)	Unavailable		**Sample Preparation:** Florisil cartridge sampling followed by solvent elution. ($10m^3$ sampling volume) **Instrumental Measurement:** GC/ECD TBB used as method surrogate. A total of 76 individual isomers analyzed. Results obtained for each congener groups (total of 8, from 2 chlorine to 9 chlorine) reported. PCB total calculated by summarizing amount of 76 isomers. MOEE Method Reference: E3125B
PCB 2		90	
PCB 3		90	
PCB 4		90	
PCB 5		90	
PCB 6		90	
PCB 7		90	
PCB 8		90	
PCB 9		90	

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

8.5.4 Phenolic/Acidic Compounds - Since the MOEE laboratory does not conduct this analysis for air samples, no guidelines are provided in this document.

8.5.5 Polycyclic Aromatic Hydrocarbons (PAHs) - Analytical Guidelines and Method Detection Limits (MDLs) for Air

Polycyclic Aromatic Hydrocarbons (PAH) - Base Neutral Extractables	CAS#	MDL*	Method Guidelines
		Air (ng/m^3)	
Acenaphthene	83-32-9	0.6	**Sample Preparation:**
5-nitro Acenaphthene	602-87-9	-	XAD - 2 resin cartridge sampling (typically in
Acenaphthylene	208-96-8	0.6	$600m^3$) soxhlet extraction.
Anthracene	120-12-7	0.6	
Benz(a)anthracene	56-55-3	0.3	**Instrumental Measurement:**
Benzo(b)fluoranthene	50-32-8	0.6	GC/MS at least 3 surrogates added prior to
Benzo(b)fluoranthene	205-99-2	0.6	sample preparation/clean-up
Benzo(g,h,i)perylene	191-24-2	0.6	
Benzo(k)fluoranthene	207-08-9	0.6	MOEE Method Reference: E3124B
Camphene	79-92-5	-	
1-Chloronaaphthalene	90-13-1	-	
2-Chloronaphthalene	91-58-7	0.6	
Chrysene	218-01-9	0.6	
Dibenz(a,h)anthracene	53-70-3	0.6	
Fluoranthene	206-44-0	0.3	
Fluorene	86-73-7	0.3	
Indeno(1,2,,3-cd)pyrene	193-39-5	0.3	
Indole	120-72-9	-	
1-Methylnaphthalene	90-12-0	0.6	
2-Methylnaphthalene	91-57-6	06	
Naphthalene	91-20-3	0.6	
Perylene	198-55-0	0.6	
Phenanthrene	85-01-8	0.6	
Pyrene	129-00-0	0.6	

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

Pesticides/Herbicides	CAS#	MDL*	Method Guidelines
		Air (ng/m^3)	
Aldrin	309-00-2	0	**Sample Preparation:**
Chlordane		-	Hi-vol. XAD-2 resin cartridge, (sampling
O,P-DDT	789-02-6	10	typically 2000 m^3), soxhlet extraction.
P,P-DDT	50-29-3	10	
DDE	72-55-9	10	**Instrumental Measurement:**
DDD	72-54-8	10	GC/MS, Dual column GC/ECD
Dieldrin	60-57-1	10	
Endrin	72-20-8	-	MOEE Method Reference: E3275A
Endosulfan I	959-98-8	-	
Endosulfan II	33213-65-9	-	
Endosulfan III	1031-07-8	10	
Heptachlor	76-44-8	-	
Heptachlor epoxide	1024-57-3	10	
Hexachlorobenzene	118-74-1	-	
Hexachlorobutadiene	87-68-3	10	
Hexachlorocyclohexane, gamma (Lindane)	58-89-9	10	
		-	
Hexachloroethane	67-72-1	-	
Methozychlor	72-43-5	-	
Toxaphene	8001-35-2	-	
Trichlorobenzene		-	

Diazinon Methyl Parathion Parathion	333-41-5 298-00-0 56-38-2	- - -	**Sample Preparation**: Solvent extraction using appropriate technique. **Instrument Measurement**: GC/MS, Dual column GC/TSD, NPD
Carbaryl	63-25-2	-	**Sample Preparation**: Solvent extraction using appropriate technique. **Instrument Measurement**: HPLC/UV
Silvex 2,4, D	93-72-1 94-75-7	- -	**Sample Preparation**: Solvent extraction using appropriate technique. **Instrument Measurement**: GC/MS, Dual column GC/ECD

*MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

PARAMETERS	CAS#	MDL ($\mu g/m^3$)		Method Guidelines
		Air Glass Fibre	Air Quartz	
Copper		0.025	0.01	Glass Fibre:
Nickel		0.025	0.01	Portion of sample digested in
Zinc		NA	0.025	H_2O:HF:HNO_3 (1:1:1) to dryness. Sample
Cadmium		0.005	NA	mode to volume with dilute acid and
Cobalt		0.025		analyzed by AAS using matrix matched
Chromium		0.10	0.01	standards.
Lead		0.01	0.05	MOEE Method Reference: E3070
Iron		1.0	0.05	
Manganese		0.01	0.01	
Aluminium		0.025		Quartz:
Sodium				
Potassium				47 mm circle cut from filter and analyzed
Calcium			0.05	by EDXRF.
Magnesium				MOEE Method Reference: E3277
Vanadium		0.025	0.025	
Molybdenum				
Barium			0.5	
Beryllium				
Strontium			0.025	
Boron				
Thallium				
Silver				
Zr			0.1	
Ti			0.02	

MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

PARAMETERS	CAS#	MDL*	Method Guidelines
		Air ($\mu g/m^3$)	
Sulphate Nitrate Chloride		0.1 0.1 0.1	Water extraction followed by ion chromatographic analysis MOEE Method Reference: E3004A
Arsenic Selenium Antimony		0.001 0.001 0.001	Digest with nitric:sulphuric:perchloric (6:3:1) acid mixture. Cool and add hydrochloric acid. Analysis by hydride flameless AAS. MOEE Method Reference: E3088A
Uranium		0.001	Digestion with nitric acid and analysis by ICP-MS MOEE Method Reference: E3212A

MDLs cited are for low level concentrations. For higher levels, MDLs should be about 1/10 of the appropriate numeric criteria from the guidelines (MOEE, 1996).

9. DATA INTERPRETATION AND REPORT CONTENT

9.1 Data Interpretation

Data interpretation should seek to ensure that the conclusions derived from the results of the study are consistent with, and support the initial aims. For most studies, the primary goal of data interpretation is to establish the existing conditions with respect to chemical concentrations of contaminants. If concentrations of certain contaminants are found to be anomalously high in relation to adjacent areas, the interpretation should seek to determine the sources.

Data interpretation should proceed through a number of steps.

1. compare results among stations
2. compare results to established guidelines
3. compare patterns of contamination
4. establish linkages to sources
5. establish linkages between chemical concentrations and the potential for biological effects

The results of most data interpretation are not definitive and the conclusions are mainly drawn on the basis of the weight of evidence that supports the conclusions. In many cases a number of supporting tests or analyses may be required and, as such, conclusions should be based on a combination of the above approaches.

1) Comparison of Results Among Stations

The first step in data interpretation consists of comparison of results among stations. By comparing results from impacted areas with unimpacted areas, the relative degrees of contamination can be determined.

Differences or similarities can be evaluated using:

i descriptive analysis, including graphs, etc.
ii statistical analyses
- simple statistics
- multivariate analyses
iii mapping (e.g., GIS) to plot contours, areas of effect, hotspots, etc.

i) Descriptive analysis.

Descriptive analysis encompasses all narrative analysis that compares or contrasts the chemical and biological findings among stations. It excludes statistical analysis which is not narrative.

· Narrative analysis of results. This generally consists of a description of chemical

concentrations, noting high and low concentrations, their locations within the study area, and their relationships to physical features (e.g., substrate type, depth, temperature).

- Comparison with other areas/localities. Results are compared with other stations within the sampling area or with stations in other similar localities.

- Graphical analysis (presentation of findings using graphs, etc) noting distribution in the study area in relation to physical characteristics and also their relationships to sources.

ii) Statistical Analysis

A number of statistical techniques are suitable for analysis of chemical, physical and biological information:

- Simple statistical tests such as t-test, ANOVA. Stations are compared and, where suitable data is available, differences in means can be tested using these statistical tests. Since in most studies the data distribution is seldom normal, statistical analysis will usually require either non-parametric tests or data transformation.

- Multivariate analyses (e.g. Principal Components, Factor Analysis, etc) can be used to relate variables among a large number of stations. Usually used to group stations that are similar on the basis of the test variables selected. Validity of the analysis depends on the variable selected.

- Suitable statistical analyses are described in Ripley, 1981 and Legendre and Legendre (1983).

iii) Mapping

One of the greatest aids to interpreting contaminant distributions within an area is through plotting the distribution of contaminants on a map. Typically, though not necessarily, this involves the use of computer systems (e.g. GIS). Most of the programs available (e.g., SPANS, RAISON) will plot data and, by making use of built-in algorithms, will draw contours, etc. This type of analysis will find extensive use where intensive sampling is involved and areas of materials to be removed or that are adversely affected need to be defined.

2) Comparison of Results to Established Guidelines.

The guidelines contain criteria for soils against which observed values can be compared. In addition, for sediments and groundwater where chemical concentrations are elevated above local background concentrations (i.e. upstream), results will be compared to the criteria in the guidelines.

3) Comparison of Patterns of Contamination

In many areas where point sources of contaminants are a concern, more than one contaminant is often involved. Data interpretation should seek to establish where and to what degree relationships between different contaminants exist.

- Includes use of correlation statistics among different parameters. These can relate the occurrence of one contaminant with that of another, and may be useful where more than one contaminant is or has been released from a source.

- Can involve correlation of chemical contamination with physical characteristics of the area. Can test whether chemical parameters are related to physical parameters such as grain size in soils and sediments.

4) Establish Linkages to Sources

This will require familiarity with the sources and the detailed industrial processes, as well as the behaviour of the contaminant in each media (water, sediment soil, and air).

- Direct cause-effect relationships between contamination and sources can be difficult to establish. Presence of compound in a known discharge area and absence or significantly lower concentrations outside is usually best link that can be achieved.

- Requires data on sources, processes used in the sources, fate and effects of the compounds.

- May require use of statistical tests to help establish the validity of these relationships.

9.2 Report Content

The final report(s) should stand alone to summarize all aspects of the decommissioning, or remediation. The report(s) should include, as a minimum, the following information:

- details on the results/findings of the Phase 1 Environmental Site Assessment

- details of the Phase 2 ESA, outlining the contaminants and wastes found at the site, including location, possible sources for this contamination and concentration; results of all analyses conducted must be reported

- information on contaminants remaining at the site, including location, concentration, persistence and migration

- an outline of the work plan undertaken to remediate or remove contaminated soil and wastes

- detailed summary of all monitoring conducted at the site including the Phase 2 study, verification sampling program and air quality monitoring report, all sampling locations should be clearly indicated on a scaled drawing

- a summary of any events or spills during the remediation

- if materials were removed from the site, a listing of the volumes and nature of these materials and disposal locations

Details on the requirements for reporting all aspects of the remediation process can be found in the main guideline document (MOEE, 1996).

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APPENDIX A: Estimation of Analytical Method Detection Limits (MDL)

ONTARIO MINISTRY OF ENVIRONMENT AND ENERGY

ESTIMATION OF ANALYTICAL METHOD DETECTION LIMITS (MDL)

Analytical Method Detection Limits Protocol

For

Municipal and Industrial Strategy for Abatement (MISA)

Program

Printed January 1988
Reprinted November 1989
Reprinted December 1990
Revised August 1994

ANALYTICAL PROTOCOL

The requirements listed in this document are specific to the Effluent Monitoring and Effluent Limits Regulations, but the principles listed here should be applied to all MOEE programs involving low-level data.

INTRODUCTION

This protocol has been established to ensure a consistent approach to the development of method detection limit (MDL) estimates for the MISA program based on the use of fortified reagent (blank) water or evaluation of available routine within-run duplicate analyses. The Effluent Monitoring and Effluent Limits Regulations have established criteria for maximum permitted laboratory MDLs (LMDLs), which are referred to as Regulation MDLs (RMDLs) and are shown in Table 1 of the "Protocol for Sampling and Analysis of Industrial/Municipal Wastewater, August 1994".

It should be noted that when MDL estimates are developed using clean samples (i.e. reagent (blank) water) they represent an optimum achievable value. MDLs obtained in this fashion are very useful for establishing performance criteria and allowing comparison of inter-laboratory method capabilities, but may not be applicable in defining the quantitation capability for other samples which introduce matrix effects.

The following protocol represents a modification to that documented in the Federal Register/Vol. 49, No. 209/Friday, October 26, 1984/Appendix B to Part 136 - Revision 1.11.

This modification restricts the options listed in the original document and gives more direct instructions at other option points.

DEFINITION

The method detection limit (MDL) is a statistically defined decision point such that measured results falling at or above this point are interpreted to indicate the presence of analyte in the sample with a specified probability, and assumes that there are no known sources of error in identification or biases in measurement.

For the purposes of this protocol, the MDL is defined as having a confidence limit of 99%. This confidence limit defines the multiplication factor used from Student's t-tables relating MDL to the analytical precision. This Student's t-value depends on the amount of data used to calculate the analytical precision. In general, analytical

precision will depend on the analytical conditions and the sample matrix. When possible, precision will be determined by replicate analysis of typical low-level samples, with sufficient replication to provide a reasonable estimate.

SCOPE AND APPLICATION

This protocol is designed for application to a wide variety of sample types ranging from reagent (blank) water fortified with a known concentration of analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The protocol requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

Since the MDL procedure was designed for application to a broad variety of physical and chemical methods, it was made device or instrument independent.

There are four options available for estimating the analytical precision:

a) accumulation of a large number of in-run duplicate analyses of typical samples at levels not exceeding 10 times the estimated MDL;

b) accumulation of in-run duplicate analyses of laboratory reagent quality water spiked with a known amount of the target analyte(s) at levels not exceeding 10 times the estimated MDL;

c) analysis of eight replicate aliquots of a typical low level sample at levels not exceeding 10 times the estimated MDL;

d) analysis of a series of eight replicate aliquots of laboratory reagent quality water spiked with a known amount of the target analyte(s) at a level not exceeding 10 times the estimated MDL.

When applied for the Effluent Monitoring and Effluent Limits Regulations, the appropriate RMDL shall be used in place of the 'estimated MDL' in the above options.

ORGANIC ANALYTES (Analytical Test Groups 16-24, 26 and 27)

This protocol requires that option d) be used. The fortification of laboratory reagent (blank) water with a known level of analyte is required to standardize the protocol for all laboratories and minimize the problems associated with analyzing duplicate or replicate samples or finding a standard "matrix" for organics analysis. The analytical precision is established based on eight replicate analyses and the estimated MDL is derived from a combination of these measurements and the appropriate value from t-test tables. This option is not intended to assess the effect of the matrix on the values obtained but rather

to define a standardized approach in the development and application of inter-laboratory performance criteria for the program.

CONVENTIONALS, METALS AND INORGANICS (Analytical Test Groups 1-15 and 25)

This protocol allows any of the options a), b), c) or d) to be used. For option a) the laboratory should review recent data on in-run duplicates (data accumulated within the preceding 12-month period or less) and apply the formula as outlined in Step 5. b) to at least 40 data pairs. The formula in Step 5. b) also applies to option b). For options c) or d) steps 1 through 5 should be followed.

PROCEDURE FOR LMDL DETERMINATION

Step 1:

Make an estimate of the detection limit using one of the following:

- The concentration value that corresponds to an instrument signal/noise of 3:1.
- The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.
- That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.
- Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

Step 2.

Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference-free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix. The use of commercially obtained or laboratory prepared organic free water or cold potable tap water is acceptable but clearly indicate what was used.

Step 3.

a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least 5 times, but not to exceed 10 times the estimated method detection limit. Proceed to Step 4.

b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated method detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated method detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated method detection limit.

If the measured level of analyte is greater than 5 times the estimated method detection limit, there are two options.

i) Obtain another sample with a lower level of analyte in the same matrix if possible.

ii) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

Step 4.

Take eight aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units.

If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. Calculate a result (x) for each sample/blank pair.

Step 5.

a) For option c) and d), 8 replicates of a typical low level sample or spiked reagent water, calculate the standard deviation (S) of the replicate measurements as follows:

$$S = \sqrt{\left[\frac{\Sigma (x_i - \bar{x})^2}{(n - 1)} \right]}$$

where:

x_i = the analytical results in the final method reporting units for the eight replicate aliquots (i = 1 to 8)

$\bar{x}$ = the average of the eight replicate measurements

b) For option a) and b), assessment of historic within run duplicate analysis data, calculate the standard deviation (S) of the duplicate measurements as follows:

$$S = \sqrt{\left[\frac{\Sigma (x_1 - x_2)_i^2}{(2 n)} \right]}$$

where:

x_1, x_2 = the two replicate results for each of the n duplicate pairs (minimum n = 40)

Compute the MDL as follows:

$$MDL = t_{(n-1, \alpha = 0.01)} S$$

where:

$t_{(n-1, \alpha = 0.01)}$ is the Student's value appropriate for a 99% confidence level given the degrees of freedom n-1.

S = the standard deviation as determined above.

Tables of Student's t Values at the 99 Percent Confidence Level

Number of Replicates	Degree of Freedom	t (n-1)
7	6	3.143
8	7	2.998
9	8	2.897
10	9	2.821
11	10	2.764
16	10	2.603
21	20	2.528
26	25	2.485
31	30	2.457
∞	∞	2.369

Recording

Record the calculated MDL to two significant figures (e.g. 0.032). The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also record the mean recovery.

Treatment of Outliers

Single Analyte Methods:

If one of the results can be shown to be an 'Outlier' by the Dixon test (described below), AND the LMDL calculated for the remaining seven replicates (3.143 times S) is less than RMDL, this latter estimate of LMDL will be accepted.

Scans:

Certain methods permit analysis of several analytes within a single 'scan'. The MDL for each analyte in the scan must be less than the corresponding RMDL. When the LMDLs tend to bracket the RMDLs, the overall method is not sensitive enough and the LMDLs will not be considered acceptable.

However, if only a few of the LMDLs in a 'scan' exceed their respective RMDLs, there may be outliers within the set of eight replicates for these non-complying analytes. If this can be confirmed, as described above, for each of the non-complying analytes, then the LMDL based on seven replicates (3.143 times S) will be accepted for those few analytes.

To forestall the possibility that one replicate sample may be an outlier for all or most analytes in the scan, and that the calculated LMDLs therefore will be greater than RMDL for several analytes, the analyst may choose the following option:

- Perform eleven replicates (rather than eight);
- For each analyte, note which replicate gives the highest and the lowest results;
- Reject the sample replicate containing the greatest number of high results;
- Reject the sample replicate containing the greatest number of low results;
- Reject the sample with the greatest number of high and low results; and
- Calculate LMDLs for each analyte using the remaining eight replicate samples.

If this procedure fails to indicate an LMDL for each analyte which is below the respective RMDL, redefine the method (for example, larger sample aliquot, different range expansion, etc.), retrain staff, and repeat the entire procedure for estimating RMDL for all analytes in the scan. Discard all previous replicate data.

Outlier procedure: Dixon's Test for sample size; n = 8 to 10.

i) sort the replicate values from lowest to highest r_1, r_2,.....$r_{(n-1)}$, r_n;

ii) determine the difference between the suspect value and the next to last value and its nearest neighbour $r_1 - r_2$ (or $r_n - r_{(n-1)}$);

iii) determine the difference between the suspect value and the next to last value at the opposite end of the sorted list of values $r_1 - r_{(n-1)}$, (or $r_n - r_2$);